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THE AMERICAN CHEMICAL SOCIETY.

I.—Proceedings.

Regular Meeting, Thursday, January 8, 1880.

The Society was called to order at 8:30 P. M., Dr. A. R. Leeds in the chair.

The minutes of the previous meeting were read and approved.

Messrs. Stillwell and Goldmark were appointed tellers by the Chair to take votes in the election of Mr. C. Semper, and they reported him duly elected member of the Society.

Mr. P. Casamajor, Corresponding Secretary, read a letter from Dr. F. A. Genth, thanking the Society for his election as President, and accepting the office.

Mr. Everett B. Bragg was proposed as member by Messrs. C. A. Goessmann, H. Endemann and E. Waller, and Mr. J. V. V. Boraun was proposed as associate, by Messrs. P. Casamajor, H. Endemann and E. Waller.

Dr. E. Waller, Librarian, read a brief statement regarding additions to the library, after which the following papers were read:

1. "Contributions to the Examination of Eastern, Western and Southern Corn," by Dr. C. A. Goessmann (read by title).

2. "The Effect of Alumina Salts on the Gastric Juice, in the Process of Digestion," by H. A. Mott, Jr., Ph. D.

3. "Analysis of the Ashes of Certain Weeds," by F. P. Dunnington.

4. "Contributions from the Laboratory of the University of Michigan," by Prof. A. B. Prescott.

Mr. Jas. H. Stebbins, Jr., made some remarks on his paper read at previous meeting, and wished to change the title of that paper. After which the Society adjourned.

ARTHUR H. ELLIOTT,
Recording Secretary.

Additions to the Library of the American Chemical Society.

From September 1st, 1879, to January 1st, 1880.

PRESENTED BY AUTHOR.

Presented by M. A. Boutlerow:

"Condensation des Hydrocarbures de la Série Éthylénique. Part 3, Sur l'Isotributylene." Pamphlet.

Presented by J. Lawrence Smith:

"Mémoire sur le Fer Natif du Groenland et sur la Dolérite qui le renferme." Pamphlet.

Presented by H. A. Mott, Jr., Ph. D.:

"Chemists' Manual."

"Adulteration of Milk." Pamphlet.

"Testing the Value of Guns by Firing under Water." Pamphlet.

"Potassium: Its Salts and Combinations." Pamphlet.

"Complete History and Process of Manufacture of Artificial Butter." Pamphlet.

"Process for the Manufacture of Illuminating Gas: History and Application."

"The Common Sense of the Salt Question." Pamphlet.

Presented by P. Schweitzer, Ph. D.:

"Various Methods of Separating and Determining Barium, Strontium and Calcium." 2 Pamphlets: parts 1 and 2.

"On the True Composition of Coal, and on the Methods of Arriving at it."

"The Water Supply of Columbia, Boone Co., Mo." Pamphlet.

"A Lecture on Petroleum." Pamphlet, 2 copies.

ACQUIRED BY GIFT.

Presented by Prof. C. F. Chandler, Ph. D.:

"Reports of the Commissioners of the United States to the International Exhibition held at Vienna, 1873." 4 vols.

Presented by Dr. E. Waller:

"Annales du Génie Civil." 6 vols: 1873–8.

"Le Technologiste." 8 vols: 1874–8.

Presented by H. A. Mott, Jr., Ph. D.:

Eugene A. Smith: "Geological Survey of Alabama." Pamphlets: 1874–5–6.

"British Husbandry." 3 vols.

M. Vernois et A. Becquerel: "Du Lait chez la Femme."

Vernois et Becquerel: "Analyse du Lait des Principaux Types de Vache, Chèvre, Brébis, Bufflesse." Pamphlet.

T. A. Quevenne: "Mémoire sur le Lait."

M. Bouchardat et T. A. Quevenne: "Du Lait."

A. Parmentier et M. Déyeux: "Précis d'Expériences et Observations sur les Différentes Espèces de Lait."

Anderson, Twamley, Desmarets, etc: "Art de Faire le Beurre et les Meilleurs Fromages."

Rudolph Wagner: "Handwoerterbuch der Physiologie." Zweiter Band: 1850.

Benno Martiny: "Die Milch." 2 vols: 1872.

Dr. Gustav Heppe: "Praktische Duengstafel." 1869. Pamphlet.

Emil Wolf: "Die Mittlere Zuzammensetzung der Asche." Pamphlet.

Oscar Cordel: "Die Stassfurter Kalisalze in der Landwirthschaft." Pamphlet.

"Ein Nachtrag zu dem Aufsatz ueber die wichtigsten Stassfurter Kaliduenger." Pamphlet.

Presented by Havemeyer & Elder:

"Dingler's Polytechnisches Journal." Vols. 227 to 230.

Presented by Dr. M. Alsberg:

R. W. Raymond: "Mineral Resources West of the Rocky Mountains." 3 vols: 1873–4–5.

Presented by A. R. Ledoux:

"Annual Report of the North Carolina Agricultural Experiment Station, for 1879."

Presented by the Scovill Manufacturing Co.:

"Photographic Times." Vol. 9: 1879.

Presented by John S. Lipps:

"Tovey's Official Internal Revenue Directory of United States and Canada Breweries."

Presented by MARIANO BARCENA:

"Boletin del Ministerio de Fomento de la República Mexicana." Vol. 4, Nos. 100 to 124.

ACQUIRED BY EXCHANGE.

With the American Academy of Arts and Sciences:

"Proceedings." Vol. 14: May, 1878, to May, 1879.

With the American Institute of Mining Engineers:

"Advance Sheets of Papers Read at the Baltimore and Pittsburgh Meetings." 1879.

"Transactions of the American Institute of Mining Engineers." Vol. 7: 1879.

With the K. K. Geologischen Reichsanstalt:

"Jahrbuch." 1879.

With l'Académie Impériale des Sciences de St. Petersbourg:

"Bulletin." Vol. 25.

With the Publishers:

"New Remedies." Vol. 5, except Nos. 7 and 9; Vol. 6, except No. 2; and Vol. 7.

"Analyst." Vol. 4: 1879.

ACQUIRED BY PURCHASE.

"Jahresbericht ueber die Fortschritte auf dem Gesammtgebiete der Agricultur Chemie." Vols. 16 to 20. "General Register ueber Jahrgang 1–20 (1858–77)."

Dr. Hermann v. Fehling: "Neues Handwoerterbuch der Chemie." Vols. 1 and 2; Vol. 3, Nos. 1 to 6.

Fittica: "Jahresbericht." 1877, part 3; 1878, parts 1 and 2.

O. L. Erdmann: "Journal fuer Praktische Chemie." New Series. Vols. 17 to 20.

NEW EXCHANGES.

AMERICAN.

"American Chemical Journal."

"Manufacturers' Review and Industrial Record."

"Medical Record."

"Sanitarian."

"Scientific American Supplement."

ENGLISH.

"Engineering."

FRENCH.

"Le Moniteur de Produits Chimiques et de la Droguerie."

GERMAN.

"Correspondenz-blatt des Vereines Analytischer Chemiker."
"Verhandlungen der K. K. Geologischen Reichanstalt."

ITALIAN.

"Gazzeta Chimica Italiana."

SPANISH.

"La Gaceta Industrial."

MEXICAN.

"Revista Cientifica Mexicana."

SOCIETIES WHICH EXCHANGE WITH THE AMERICAN CHEMICAL SOCIETY.

AMERICAN.

Academy of Natural Sciences.
American Academy of Arts and Sciences.
American Institute of Mining Engineers.
American Philosophical Society.
American Society of Civil Engineers.
National Association of Wool Manufacturers.
New York Academy of Sciences.

ENGLISH.

Chemical Society.
Newcastle-on-Tyne Chemical Society.
Pharmaceutical Society of Great Britain.
Society of Arts.

FRENCH.

Societé d'Encouragement pour l'Industrie Nationale.
Societé Industrielle d'Amiens.
Societé Industrielle de Mulhause.
Societé Industrielle de Rouen.

GERMAN.

Deutsche Chemische Gesellschaft.
Kaiserliche Akademie der Wissenschaften in Wien.
K. B. Akademie der Wissenschaften zu Muenchen.
K. K. Geologischen Reichanstalt.

RUSSIAN.

Académie Impériale des Sciences de St. Petersbourg.

DEPARTMENTS OF THE U. S. GOVERNMENT WHICH EXCHANGE WITH THE AMERICAN CHEMICAL SOCIETY.

Bureau of Statistics.

National Board of Health.

CONTRIBUTIONS TO THE MUSEUM SINCE THE FOUNDATION OF THE SOCIETY.

Presented by W. H. NICHOLS:

Piece of lead lining of tank, showing a peculiar corrosive action of Artesian well water. Taken from the Sulphuric Acid Works of G. H. Nichols & Co., on Newtown Creek, Long Island.

Specimen of flue dust taken from Sulphuric Acid Works.

Presented by Dr. M. ALSBERG:

Series of twelve specimens illustrating the manufacture of bronze powders from the ingot.

Specimen of artificial cinnabar.

Presented by J. P. BATTERSHALL, Ph. D.:

Specimen of fibrous sodic chloride found in a cargo of Peruvian guano.

Presented by MARIANO BARCENA:

Specimen of livingstonite (Barcena), sulphide of antimony and mercury. From Huitzuco, Mexico.

Specimen of pipitzaboic acid, extracted from the Mexican plant called *Trixis pipitzaboae.*

Presented by Prof. J. W. MALLETT:

Specimen of heptane, first obtained as a distillate from the exudation of *Pinus sabiniana*, by Mr. Wm. T. Wenzell, of San Francisco, Cal., and described by him under the name of "Abietene."

Two specimens of China galls, *Rhus semialata.*

Specimen of Japan galls.

Presented by Messrs. E. S. MOFFAT and PARDEE:

Two specimens of magnetic iron ore, one containing 15 per cent. MgO as serpentine. From Libby Foster Mine, New York State.

Specimen of hematite ore from Bilboa, Spain.

Specimen of hematite ore from Mockta, Algeria.

Presented by E. M. JOHNSON:

Specimens of ferro-chromium, showing fracture, and containing from one-eighth per cent. to 2.9 per cent. of chromium.

Three specimens of chrome steel, showing fracture.

Specimens of ferro-chromium containing 36.54 per cent. of chromium.

Presented by G. H. JOHNSON:

Specimen of ferro-manganese containing 88.68 per cent. of manganese.

Specimen of German ferro-manganese containing 29.05 per cent. of manganese.

Alloy containing 83.79 per cent. of manganese.

Presented by Messrs. PICKHARDT & KUTTROFF:

Case containing sixty-six samples of aniline dyes.

Presented by T. E. ALLEN:

Specimen of common salt showing ripple marks, taken from the shore of Great Salt Lake, Utah.

E. WALLER, Ph. D.,
Librarian.

II.—CONTRIBUTIONS TO THE EXAMINATION OF EASTERN, WESTERN AND SOUTHERN CORN.

By Prof. C. A. GOESSMANN, Mass. Ag'l Coll.

This investigation was undertaken at the request of several Agricultural Societies of the Connecticut River Valley, in Massachusetts, to ascertain the relative feeding value of corn.

Sweet Corn.

I.—"TEXAS BLUE SWEET," Palmer, Mass.

The ear contained eight rows of kernels of a blue color; its average length was from 5 to 6 inches, and its average weight was

from 3 to 4 ounces, consisting of 88 per cent. of kernels and 12 per cent. of cob. The average weight of one kernel was 0.32 grm.

The corn was raised upon rich garden soil, manured with commercial fertilizers.

II.—"CROSBY," Greenfield, Mass.

The ear contained fourteen rows of kernels of a white color; its average length was from 7 to 8 inches; its average weight was from 4 to 5 ounces, and consisted of 79 per cent. of kernels and 21 per cent. of cob. The average weight of one kernel was 0.2 grm.

The corn was raised upon rich garden soil, manured with commercial fertilizers.

Indian Corn (*Maize*).

I.—"WHEELER'S PROLIFIC," West Springfield, Mass.

The ear contained eight rows of kernels of a yellowish-brown to brown color; its average length was from 7 to 11 inches; its average weight was from 7 to 8 ounces, and consisted of 83 per cent. of kernel and 17 per cent. of cob. The average weight of one kernel was 0.438 grm.

The corn was raised upon a light sandy loam, manured with commercial fertilizers.

II.—"CLARK," North Hadley, Mass.

The ear contained eight rows of kernels of a yellow color; its average length was 9 inches; its average weight, 6 to 7 ounces, and consisted of 86 per cent. of kernels and 14 per cent. of cob. The average weight of one kernel was 0.4 grm.

The corn was raised upon a sandy loam, manured with commercial fertilizers. For six or seven years previously, grass had been raised on the land, without manure.

III.—"TIP CORN," Chicopee, Mass.

The ear contained eight rows of kernels of a yellow color; its average length was about 7 inches; its average weight from 4 to 5 ounces, and consisted of 87 per cent. of kernels and 13 per cent. of cob. The average weight of one kernel was 0.3 grm.

The corn was raised upon "river land," manured with barn-yard manure.

IV.—"SOUTHERN WHITE FLINT," South Carolina.

The ear contained twelve rows of kernels of a white color; its average length was 8.5 inches; its average weight, about 7 ounces,

and consisted of 80 per cent. of kernels and 20 per cent. of cob. The average weight of one kernel was 0.29 grm.

The corn was raised upon a light sandy soil, without manure.

V.—"CANADA DUTTON," Mass. Ag'l Coll., Amherst, Mass.

The ear contained twelve rows of kernels of a yellow color; its average length was 9.5 inches; its average weight, from 8 to 9 ounces, and consisted of 82 per cent. of kernels and 18 per cent. of cob. The average weight of one kernel was 0.3 grm.

The corn was raised upon a sandy loam, manured with barn-cellar manure; 56 cords per acre.

VI.—"CANADA DUTTON," Sunderland, Mass.

The ear contained twelve rows of kernels of a dark yellow color; its average length was from 9 to 10 inches; its average weight from 7 to 8 ounces, and consisted of 84 per cent. of kernels, and 16 per cent. of cob. The average weight of one kernel was 0.3 grm.

The corn was raised upon a light alluvial soil, river land, manured with barn-yard manure; 10 cords per acre.

VII.—"EARLY SOUTHERN," Hatfield, Mass.

The ear contained sixteen rows of kernels of a light yellow color; its average length was from 10 to 11 inches; its average weight was from 15 to 16 ounces, and consisted of 82 per cent. of kernels, and 18 per cent. of cob. The average weight of one kernel was 0.46 grm.

The corn was raised upon Connecticut River bottom land, in a high state of cultivation, as tobacco had been the crop the previous year.

VIII.—"WESTERN DENT" (white), Mt. Palatine, Ill.

The ear contained sixteen rows of kernels of a white color; its average length was 8.5 inches; its average weight was about 10 ounces, and consisted of 84 per cent. of kernels, and 16 per cent. of cob. The average weight of one kernel was 0.3 grm.

The corn was raised upon black loam (prairie land), which had never been manured.

IX.—"WESTERN DENT" (yellow), Mt. Palatine, Ill.

The ear contained from twenty to twenty-four rows of kernels of a yellow color; its average length was about 8 inches; its average weight was from 12 to 13 ounces, and consisted of 86 per cent. of kernels, and 14 per cent. of cob. The average weight of one kernel was 0.3 grm.

The corn was raised upon black loam (prarie land), which had never been manured.

SUMMARY OF ANALYSES OF CORN (*Kernels*).

Number of Sample.	Moisture.	Fat.	Nitrogenous Matter. (Albuminoids.)	Non-nitrogenous Extractive Matter.	Cellulose.	Ash.
			Sweet Corn.			
I.	10.000	8.487	13.515	63.957 Including 1.83 per c't. of grape sugar and 4.23 per c't. of cane sugar.	2.500	1.541
II.	10.000	6.950	11.670	67.109 Including 2.14 per c't. of grape sugar and 8.15 per c't. of cane sugar.	2.500	1.770
			Indian Corn (Maize).			
I.	10.000	4.720	12.432	69.518	1.890	1.440
II.	10.000	4.860	12.420	68.560	2.560	1.660
III.	10.000	5.194	12.703	68.063	2.500	1.540
IV.	10.000	4.480	12.463	69.667	2.020	1.370
V.	10.000	4.747	12.489	68.928	2.500	1.336
VI.	10.000	5.251	10.847	69.971	2.500	1.431
VII.	10.000	4.975	11.925	68.900	2.500	1.700
VIII.	10.000	4.266	11.529	70.323	2.500	1.382
IX.	10.000	4.545	11.115	69.799	3.041	1.500

The cellulose has been ascertained, by actual test, in I., IV., IX. (Maize); in the remaining samples, the mean of these tested samples has been assumed.

ANALYSES OF THE ASH OF SOME OF THE ABOVE VARIETIES OF CORN (*Kernels*).

One hundred parts of the ash contain:	II. Crosby's Sweet.	I. Wheeler's Prolific.	IV. Southern White Flint.	V. Canada Dutton.	III. Canada Dutton.	IX. Western Dent (yellow).
Silica soluble in Soda..	1.542	1.271	0.362	0.306	0.763	2.612
Ferric oxide.....	0.195	0.934	0.789	0.977	2.087	0.331
Calcium oxide.....	1.788	1.033	1.007	1.797	1.501	1.611
Magnesium oxide.....	12.542	14.613	15.497	13.102	14.564	15.800
Potassium oxide	40.237	25.617	27.988	23.109	29.481	31.054
Sodium oxide.....	1.187	2.171	1.890	4.257	.....	3.260
Phosphoric Acid.....	42.509	53.657	52.458	55.481	51.604	45.314

Carbon, sulphur and chlorine, not determined.

SUMMARY OF ANALYSES OF CORN (*Kernels*), WITH REFERENCE TO THE DIGESTIBILITY OF ITS CONSTITUENTS.

(Nitrogenous matter, 85 per cent.; fat, 76 per cent.; non-nitrogenous extractive matter, 94 per cent.; cellulose, 34 per cent.)

No. of Sample.	Nitrogenous Matter. (Albuminoids.)	Non-nitrogenous Extractive Matter.	Fat.	Ratio of Nitrogenous to Non-nitrogenous Matter.
		Sweet Corn.		
I.	11.49	60.12	6.45	1 : 5.79
II.	9.92	65.62	5.28	1 : 7.14

No. of Sample.	Nitrogenous Matter. (Albuminoids.)	Non-nitrogenous Extractive Matter.	Fat.	Ratio of Nitrogenous to Non-nitrogenous Matter.
		Indian Corn (*Maize*).		
I.	10.57	65.35	3.59	1 : 6.52
II.	10.56	64.45	3.69	1 : 6.45
III.	10.80	63.98	3.95	1 : 6.29
IV.	10.59	65.49	3.40	1 : 6.51
V.	10.62	64.79	3.61	1 : 6.44
VI.	9.22	65.77	3.99	1 : 7.56
VII.	10.14	64.77	3.78	1 : 6.76
VIII.	9.80	66.10	3.24	1 : 7.07
IX.	9.45	65.61	3.41	1 : 7.30

The above described samples of corn rank, with reference to their feeding value, as follows:

Sweet Corn.

I.—Blue Texas Sweet Corn, Palmer, Mass.
II.—Crosby's Sweet Corn, Greenfield, Mass.

Indian Corn (*Maize*).

III.—Tip Corn, Chicopee, Mass.
V.—Canada Dutton, Mass. Ag'l Coll.
II.—Clark Corn, North Hadley, Mass.
IV.—Southern White Flint, South Carolina.
I.—Wheeler's Prolific, West Springfield, Mass.
VII.—Early Southern, Hatfield, Mass.
VIII.—Western Dent (white), Mt. Palatine, Ill.
VI.—Canada Dutton, Sunderland, Mass.
IX.—Western Dent (yellow), Mt. Palatine, Ill.

Judging from the above analyses, it is reasonable to assume:

First—that the varieties of sweet corn are, on account of their peculiar and superior composition, the most valuable kinds we have for feeding purposes.

Second—there is, apparently, no marked distinction between a good sample of Eastern and a good sample of Western or Southern corn; the Eastern corn, cultivated and harvested with better care, as a rule, than the bulk of the Western corn, seems to be the safer article.

Third—that a more or less careful system of cultivation and harvesting would cause as striking variations in the chemical composition of *every one* of the above varieties—not excepting the Western varieties—as are noticeable in the above analytical statements. A good illustration of this circumstance may be noticed in samples V. and VI., both being Canada Dutton; the former contains 12.42 per

cent. of nitrogenous matter, the latter only 10.85 per cent., a difference of 1.57 per cent., for which an increase of 0.39 per cent. of fat does not compensate. The first-mentioned sample was raised after a heavy dressing with barn-yard manure (56 cords per acre), and the latter after a light one (10 cords per acre).

SUMMARY OF ANALYSES OF CORN-COBS.

Indian Corn (Maize).

No. of Sample.	Moisture.	Fat.	Nitrogenous Matter. (Albuminoids.)	Non-nitrogenous Extractive Matter.	Cellulose.	Ash.
I.	10.0000	0.6032	3.7313	54.5226	29.8700	1.2729
IV.	10.0000	0.3406	3.1413	55.7898	30.0500	0.6783
V.	10.0000	.....	.....	.....	.....	0.1629
VI.	10.0000	.....	.....	.....	... ...	1.1485
IX.	10.0000	0.4117	3.2587	57.2537	28.2265	0.8494

ANALYSES OF THE ASH OF THE ABOVE VARIETIES OF CORN-COBS.

One hundred parts of the ash c ntain:	I. Wheeler's Prolific.	IV. Southern White Flint.	V. Canada Dutton.	VI. Canada Dutton.	IX. Western Dent (yellow).
Silica soluble in soda....	17.344	20.819	10.314	.....	25.478
Ferric oxide.....	trace.	1.249	6.687	1.822	0.621
Calcium oxide.....	2.189	3.066	2.372	4.995	2.293
Magnesium oxide.....	5.317	4.561	4.989	9.586	3.976
Potassium oxide.....	60.129	59.818	62.362	78.846	54.231
Sodium oxide	5.745	2.293	2.907	.....	8.302
Phosphoric acid.....	9.185	8.026	10.363	4.731	5.098

Carbon, sulphur and chlorine, not determined.

No actual test regarding the digestibility of the various proximate constituents of corn-cobs has yet been made; hence, their nutritive ratio has never been exactly determined. Their composition is similar to that of corn-stalks, and they compare, also, most favorably with the straws of most of our winter and summer grains. A. Stoeckhardt places dry, ground corn-cobs on an equal scale, in feeding value, pound for pound, with fresh potatoes.

III.—The Effects of Alumina Salts on the Gastric Juice in the Process of Digestion.

By Henry A. Mott, Jr., Ph. D.

The introduction of alum into flour for various purposes, has been a trick of the baker for the past one hundred years; fortunately, its introduction is limited now to a few unscrupulous bakers—as in England, France and Germany, it is an offense punishable by fine and imprisonment, to use alum in any connection with articles of food.

That alum is a poison, numerous experiments have demonstrated. The experiments conducted by Devergie and Orfila on living animals, with alum, clearly demonstrate its poisonous nature. They conclusively demonstrated that alum, in its hydrated and anhydrous (or calcined, exsiccated) condition, has a corrosive action on the mucous membrane; and, further, that it is sure to produce vomiting, constipation, extreme weakness, and loss of appetite, even in very small doses; and in such cases, if either by accident or intention, vomiting is prevented, death is sure to result.

Several cases of poisoning by the accidental use of alum have been reported from time to time. A Mrs. B., reported by Dr. Fournier, "took by mistake a swallow of about three teaspoons of a solution of 16 grms of calcined alum in a liter of water. She at once complained of nausea, severe heat, tearing pains in all parts in contact with the alum; her pulse had become rapid, and the face animated; the muscles had been agitated by slight convulsive movements; the desire to vomit had increased; the thirst had become inextinguishable."

Another case is reported by Dr. Ricquet, where a Mr. V. M., wishing to purge himself, ordered some sulphate of magnesia, but by mistake alum was given him; on dissolving 30 grains in water and drinking the same, he succumbed after horrible pains, eight hours after taking the poison.

Besides the last mentioned case of death resulting from taking alum internally, must be mentioned three cases of alum poisoning by Von Hasselt, Taylor and Husemann, and two cases by Tardieu—all of which terminated fatally.

Tardieu speaks of a woman who murdered her three months' old child by administering about 0.9 grm of alum.

When alum is used in flour in the manufacture of bread, some of the alum is decomposed by the phosphates of the flour, and phosphate

of alumina, basic sulphate of alumina, and some unaltered alum, are left in the bread. The introduction of alum as a substitute for cream of tartar in baking powders, is a recent fraud on the public, and, strange to say, has been upheld by a few men, who, it would be supposed, would condemn its introduction in the strongest terms. In an alum baking powder, another chemical change takes place—owing to the presence of bicarbonate of soda—and hydrate of alumina is formed, a very soluble modification of alumina, as compared with the phosphate or basic sulphate—but only just so much of the hydrate of alumina is formed as there is bicarbonate of soda present in the powder to form it—and as the alum is always in excess, being the acid of the compound, there is also formed phosphate of alumina, basic sulphate of alumina, and some alum is left unaltered.

Some of the manufacturers of alum baking powders have induced a few scientific men, besides saying there is no alum in the baked product, to say that the alumina hydrate of the alum is rendered insoluble by the processes of baking, and that it would pass through the system like clay, or any other inert substance.

This might seem plausible at first thought, but when we consider that it takes only ten to twenty minutes in a suitable oven to bake biscuit, and that, after the biscuit is baked, it contains, itself, about fifty per cent. of water, we see how utterly impossible it would be to drive off the water of combination of the hydrate of alumina, so as to render it insoluble, as aluminic oxide.

It hardly seems necessary for any experiments on animals to decide a question of this nature, so that the use of alum baking powders can be condemned; for a scientific consideration of the subject can lead to no other conclusion. Still, as Prof. Patrick, of Missouri, conducted some experiments on cats, to sustain his position in stating that alum baking powders are not injurious to health, I thought it advisable to conduct a series of experiments on dogs, in search of the truth.

Through the courtesy of the Commissioners of the Dock Department, I secured a shed on their premises foot of Sixteenth street and East River. This shed I had completely remodeled into a suitable house, having the dimensions of about 16x14x12 feet high. Sixteen stalls were made inside, having the dimensions of 3½ feet by 2 feet by 2½ feet. The bottom of each compartment was covered with straw, making a pleasant bed for the dogs. I then secured 16 dogs from the pound, which were all carefully examined to see if they were in a perfect state of health. None but strong, healthy dogs were selected. The breed, age, food, color and weight, of every dog

was carefully noted. Each dog was then consigned to a stall, and securely chained, and they all received a number, from one to sixteen. I commenced my experiments on the 9th of September, and finished December the 3d. My assistant was with the dogs from morning until night, and never left the animals without first securely bolting and locking the dog-house. No stranger was allowed to enter the house unaccompanied either by myself or by my assistant, and the dogs never received a mouthful of food or anything else from any one except my assistant and myself.

I will now detail the result of my experiments:

Dog No. I.

Breed—Coach.
Age—1 year.
Health—Perfect.
Food—Bread and crackers.
Color—Spotted black and white.
Weight—35 lbs.

To this dog, on the morning of the 9th of September, was given 8 biscuits, at ten minutes past eight o'clock. The biscuits were made by myself, as follows:

1 quart sifted flour; 20 teaspoons alum baking powder; 2 cups of water; 1 tablespoon of butter. 22 biscuits made, weighing 27 oz. Time of baking, 20 minutes.

At half-past eleven, the dog was taken very sick, vomiting profusely ; his vim and brightness of eye had departed, and he trembled considerably in his limbs.

At four o'clock, five more biscuits of the same nature were given, but he would not eat them.

The next morning, eight more fresh biscuits were given him; he ate only part of one. During the day previous he was quite loose in the bowels; but he had now become very constipated, and it was only with great effort and pain he was able to relieve himself for several days.

On September 11th, as he would not eat the biscuits alone, they were mixed with meat; this he ate, but remained very dejected in spirits and extremely constipated.

To dog No. V. the same food was given. The description of the dog was as follows:

Breed—Terrier.
Age—9 years.
Health—Perfect.
Food—Crackers.
Color—Brindle.
Weight—30 lbs.

At 8.15 on September 9th, eight biscuits, made as described above, were given. At 12.15, the dog became very sick and vomited profusely. At 4 P. M., five more biscuits were given him, but he would not eat. He was very constipated towards night. On the following morning, eight biscuits were given him, which he ate in part during the day; in the afternoon he was very sick, vomiting at 4.30 and again at 5.45 P. M.

Experiments were next made, using only half the quantity used above of an alum baking powder.

The biscuits were made as follows:

1 quart sifted flour; 10 teaspoons alum baking powder; 1⅞ cups of water; 1 tablespoon of butter. 27 small biscuits, weight 25½ oz. Time of baking, eleven minutes.

Three dogs were fed with biscuits thus made, with the following results:

	No. II.	No. IV.	No. VI.
Breed	Cur.	Spitz Cur.	Shepherd.
Age	15 months.	1 year.	4 years.
Health	Perfect.	Perfect.	Perfect.
Food	Bread.	Crackers.	Crackers.
Color	Black.	Yellow.	White.
Weight	16 lbs.	10 lbs.	40 lbs.

Eight biscuits were given to dogs Nos. II. and VI. in the morning; in the afternoon, dog No. II. was very loose in his bowels, and dog No. VI. very constipated. Five more biscuits were given in the afternoon, and eight more the following morning, part of which were eaten. Both the dogs then were extremely constipated and apparently quite sick, although they did not vomit. To dog No. IV., in perfect health, was then given three biscuits, which were eaten at 9 o'clock. At 10.35 A. M., the dog became quite sick and vomited. In the afternoon and next morning, more biscuits were given him, but he would not eat.

This demonstrates that some animals are more susceptible to the action of poisonous substances than others.

It now became necessary to know if the same effects would not be brought about by using the same quantities of cream of tartar powder. I therefore conducted a series of experiments to arrive at this point. Three dogs were experimented on. The following is a description of the animals:

	No. IX.	No. X.	No. XVII.
Breed	Mongrel.	Mongrel.	Terrier.
Age	4 years.	10 years.	2 years.
Health	Perfect.	Perfect.	Perfect.
Color	Black and White.	Black and White.	Black and Tan.
Weight	20 lbs.	35 lbs	15 lbs.

The biscuits were composed as follows:

1 quart sifted flour; 20 teaspoons cream of tartar baking powder; 2 cups of water; 1 tablespoon butter. 20 minutes baking. 26 small biscuits. Weight 27 oz.

The biscuits given to dog No. XI. were twice as large—only 12 being made instead of 26; therefore, each dog was given as many biscuits as he would eat, without in any way affecting them. Their bowels were not in the least affected. Each dog ate sixteen biscuits the first day, eight in the morning and eight at night. Dog No. X. ate but ten biscuits; the next day each dog ate the biscuits again with appetite. Dog No. XVII. was fed four days on the biscuits, and ate the same with appetite, without showing any signs of sickness.

These experiments clearly demonstrate that the salts left in the biscuit, when a cream of tartar baking powder is used, are perfectly harmless; but when an alum baking powder is used, are very dangerous, as in every case where dogs were fed on biscuits made with such powders, the dogs were made very sick, causing them to vomit profusely, lose all energy, and show weakness in their limbs.

The next series of experiments was to ascertain what effect would be produced by feeding dogs with hydrate of alumina mixed in with their food, as also phosphate of alumina. To two dogs, Nos. XV. and XVI., hydrate of alumina was thus given.

The following is a description of the dogs:

	No. XV.	No. XVI.
Breed	Mongrel.	Mongrel.
Age	1 year.	3 years.
Health	Perfect.	Perfect.
Food	Bread.	Bread.
Color	White.	White and Black.
Weight	18 lbs.	20 lbs.

The hydrate of alumina was prepared by Professor Schedler; it was made by precipitating the alumina in alum by means of ammonia, and then thoroughly washing the same with water until the washings were perfectly free from traces of ammonia. The precipitate was then dried between blotting paper, and analyzed to ascertain the percentage of water it contained. The following is an analysis of the same:

Hydrate of alumina	12.48 per cent.
Abnormal water	87.52 "
	100.00 "

From this analysis it will be seen that 1 ounce of the precipitate is really only $\frac{1}{8}$ oz. of hydrate of alumina, or 54½ grains. To dog No. XVI. on the 13th of September, was given 1 ounce of precipitated hydrate of alumina (54½ grains $Al_2O_3.3H_2O$) mixed with meat, at a quarter past eight in the morning. At 12.30 the dog became quite sick, and vomited; at ten minutes of six in the afternoon, ¼ oz. (109.2) more of hydrate of alumina in meat, was given to the dog, and at twenty minutes past six he was again taken quite sick, and vomited; he vomited also considerable during the night, the meat being vomited up *undigested*. The next morning, ¼ oz. (109.2 grains) more of hydrate of alumina mixed with meat, was given to the dog, and he vomited a short time afterwards; he was very constipated, his last stool being quite black. At three o'clock, 109.2 grains more were given him, and he was again taken sick, vomiting, and showing great weakness in his limbs. The next day at three o'clock, he was given ¼ oz. more of hydrate of alumina mixed with meat, when he was taken extremely sick, vomiting several times, and showing great weakness in his limbs, and loss of ambition, the brightness of eye having disappeared; he vomited during the night, and could not be induced to eat any more the next day or the day following.

To dog No. XV. was given ⅜ oz. (163½ grains) of hydrate of alumina mixed with meat. The dog was taken very sick in about two hours, and vomited just two hours and fifty minutes afterwards; he also vomited profusely during the night. At 4.30 the next day, ½ oz. (218 grains) of hydrate of alumina mixed with meat, was given the dog, but he ate only about one-half of it. He was taken very sick a short time afterwards, vomiting, and showing great weakness and restlessness. He would not eat any more after that day. It may be well to state here that hydrate of alumina is almost tasteless, and it was, for this reason, the dogs ate it as well as they did when mixed with meat. To two other dogs hydrate of alumina was given only once, and in each case the dogs were made sick, and vomited.

To dog No. IX. was given phosphate of alumina mixed with meat. The following is a description of the animal:

Breed—Mongrel.
Age—4 years.
Health—Perfect.
Food—Bread.
Color—Black and white.
Weight—20 lbs.

On September 18th, in the morning, 3 oz. of precipitated phosphate of alumina (containing 75 per cent. of water, dried between blotting

paper) was mixed with meat, and given to the dog. This was eaten during the day, but the dog did not vomit, although he was evidently quite sick. The next morning, 2 oz. more of the precipitated phosphate of alumina mixed with meat was given him, which was all eaten, and although the dog did not vomit, he was quite sick, showing less life than usual, and his eye not being as bright.

From this last experiment, it was clearly shown that the alumina in biscuits made with an alum baking powder, must be, to a very great extent, in the condition of hydrate of alumina—as the phosphate, although causing the animal to feel unwell, did not make him vomit. In every case, as has been stated before, when biscuits given to a dog, were made with less than seven times the quantity of alum baking powder usually employed, the dog vomited profusely, and was made very sick, trembling in his knees; and this was the case when hydrate of alumina was given, even in such small quantities as one-eighth of an ounce, or 54½ grains. Experiments were then made to see if the action of hydrate of alumina in any way differed from the action of alum itself. The following is a description of the dogs employed:

	XIII.	XIV.
Breed	Terrier.	Terrier.
Age	2 years.	2 years.
Health	Perfect.	Perfect.
Food	Bread.	Bread.
Color	Black and tan.	Tan.
Weight	10 lbs.	20 lbs.

To dog No. XIII. was given 2 oz. of burnt potash alum mixed with meat, at 8.15 in the morning. The dog ate only the meat, leaving the alum untouched, with the exception of what adhered to the meat, which was much less than one-quarter of an ounce. At 9.30 he was very sick, trembling in his limbs, losing all vim and brightness of eye, and vomiting. At 9.45 he vomited again. The next day some fresh meat was mixed in with the alum; when he ate part of the meat he was made very sick again, and vomited considerably. He would not eat any more after this.

To dog No. XIV. 1 oz. of ammonia alum was mixed with meat, and fed. At 8.15 only about ⅛ oz. was eaten. A 9.45 he was made very sick, the same as dog XIII., and vomited; he vomited again at 9.45 and again at 9.55, and he was a very sick dog, showing no inclination to eat or play; his brightness of eye had entirely disappeared. To two other dogs alum was given, with the same results. From these experiments it will be clearly seen that hydrate of alumina acts in the

same manner as alum, causing the animal to vomit profusely, showing great weakness in the limbs, and loss of ambition.

The next experiments were conducted to ascertain what effect the presence of alum, hydrate of alumina, phosphate of alumina, and basic sulphate of alumina, had on the solvent power of the gastric juice. It was necessary, therefore, to procure some gastric juice for experiment. I therefore sent several dogs to Prof. J. W. S. Arnold, who inserted a canula in each of them. When the dogs were in a perfectly healthy condition, Prof. Arnold sent me some gastric juice, which was produced by tickling the lining of the stomachs of the dogs with a feather or glass rod, which caused the gastric juice to flow out of the fistula into a receptacle placed underneath the dog to receive it. This and other methods were used to excite the flow of the secretion.

In conducting the experiments with the gastric juice, I was greatly assisted by the friendly services of Prof. Robert Schedler. Four samples of gastric juice were received. The following are the experiments conducted with the same.

Sample No. 1.—Obtained by irritating the lining of the stomach with a glass tube; pure and free from food. The acid was determined in this sample, and found to be 0.13388 hydrochloric acid.

Sample No. 2.—Boiled ox heart was fed to the dog, which caused a flow of gastric juice, which was afterward drawn off. The acid in this sample was only 0.006083 hydrochloric acid.

Sample No. 3.—In three grms of this juice the acid was determined and found to be 0.21268 hydrochloric acid.

Experiments were then made with this sample, as follows:

To three grms of juice was added .0403 grm of fibrine,* and the mixture kept at a temperature of 95–100° F., for half an hour, when all the fibrine was dissolved.

To three grms more of the juice wsa added 0.5 grm of hydrate of alumina (precipitated and dried between blotting paper), and then 0.0403 grm of fibrine was added. The mixture was stirred and kept at the temperature of 95–100° F. for two hours, and from 70–80° F. for twenty-three hours. Digestion of the fibrine took place at the start, but was soon arrested, only one-quarter of the fibrine being dissolved.

To three grms more of the juice was added .500 grm of alum, and .0403 grm of fibrine, and this was treated the same as in the last experiment. In this case about three-quarters of the fibrine was dis-

* The fibrine was prepared by Prof. Arnold, from the blood of a dog.

solved at the start, and then further digestion was entirely checked, although it remained in contact twenty-three hours.

These three experiments are very valuable, as fibrine is so readily dissolved. They show that both aluminic hydrate and alum can check the digestion of such an easily digested substance as fibrine. They show, therefore, how dangerous it is to introduce these two salts into our stomachs, if we do not wish to excite indigestion and dyspepsia.

Three experiments were then conducted with prepared boiled white of egg. To three grms of gastric juice was added .25 grm of albumen, and the juice was kept at 95–100° for two hours, when half of the egg was dissolved. Three more grms of the juice were then added, when in two hours all the egg was dissolved. This showed that 100 grms of gastric juice would dissolve 4.16 grms of albumen. Lehmann claims it will dissolve 5 grms, and Schmidt 3.95 grms, although the latter authority states it may dissolve more.

To three grms more of gastric juice was added .25 grm precipitated hydrate of alumina (really only .031 grm $Al_2O_3.3H_2O$), and then .25 grm albumen; the mixture was kept at the temperature of 95–100° F. for two hours, and in contact fifteen hours, and not a particle of the egg was dissolved.

To three grms more of the same juice was added .25 grm of alum, and then .25 grm of albumen, and this was likewise treated; but after fifteen hours contact not a particle of the albumen was dissolved. These experiments were duplicated.

The albumen used in the experiments was the boiled white of egg; it was first macerated in a mortar with pure water, then dipped in a solution of 1 drop of hydrochloric acid to 2,400 drops of water; it was afterwards macerated again in the mortar with pure water, then dried between filter paper, and weighed.

The three first experiments demonstrate that both hydrate of alumina and alum check the digestive properties of the gastric juice, and render it incapable of digesting even the most digestible substances; and the last three experiments demonstrate that the digestive power of the gastric juice is entirely destroyed by hydrate of alumina and alum, so far as dissolving the more indigestible substances, such as the boiled white of egg.

Experiments were next made with phospate of alumina, and basic sulphate of alumina.

To three grms of a fresh sample of gastric juice, were added 0.1 grm of phosphate of alumina and 0.1 grm of boiled white of egg.

To three grms more of the gastric juice, were added 0.1 grm of phosphate of alumina and 0.1 grm of boiled white of egg.

These two mixtures were kept between 95–100° F. for two hours, and in contact twenty-four hours, and not a particle of the albumen was dissolved in either case. These experiments were duplicated with fresh gastric juice from another dog, with the same results. These experiments show that all alumina salts interfere with the powers of digestion, having the property of rendering the pepsin inactive.

My next experiments were to ascertain whether alumina could be found in the various organs of the body, if a dog was fed with hydrate of alumina. I therefore secured a dog from Prof. Arnold, of which the following is a description:

Breed—Terrier.
Color—Black and tan.
Age—1½ years.
Weight—20 lbs.

This dog had a gastric fistula, through which the hydrate of alumina suspended in a water solution, was introduced direct into the stomach, by means of an ordinary syringe.

On the 21st of October, at 8.30 A. M., 5 oz. of precipitated hydrate of alumina and 2 oz. of meat, were mixed together, and given to the dog. He ate only one-third of the mixture; at 11.35 his bowels were very loose, and at 12.40 he vomited; at 12.55 he vomited profusely again, the meat coming up undigested.

At 5 P. M., one-twentieth of an ounce of hydrate of alumina, suspended in solution, was injected directly into the stomach. The dog vomited during the night. The next morning, at 9.25 A. M., one ounce of hydrate of alumina was injected into the stomach, and the dog was given meat to eat. He vomited at 1.30 P. M., and was very constipated; vomited at 2 P. M., and again at 2.15 P. M. At 3 o'clock, one ounce more of the hydrate of alumina was injected; at 5 P. M. he vomited; he also vomited during the night, and was very constipated. At 8.45 the next morning, about one ounce more of the hydrate of alumina was injected; he vomited at 11.45, and again at 12.55. At 4.55 P. M., one-quarter ounce more of hydrate was injected, the dog vomiting during the night. The dog now was so completely under the influence of the hydrate of alumina, that I fully believe he would have died if any more alumina was injected. He was a very sick dog, trembling in his knees when he stood up, and wanting all ambition and vim. His eye was dull, all the brightness had departed. On the next morning, at 8 o'clock, I killed the dog, collected some of his blood, and took his liver for analysis. I separated from the blood, by

analysis, a considerable quantity of alumina, as also from the liver. The silica and phosphate of lime were first removed before the alumina was precipitated.

My next experiment was on a black and tan dog in Prof. Arnold's laboratory. I supplied Prof. Arnold with freshly precipitated hydrate of alumina, and he fed the animal with 12 oz. of the same during four days, when the dog was killed. I received the kidney, heart and blood, for analysis, from all of which I separated out alumina in large quantities. Professor Arnold examined the intestinal canal, finding the upper portion of the *duodenum* much inflamed, and also analyzed the spleen and liver, proving there the presence of alumina.

The next dog experimented on was also a black and tan. To this dog Prof. Arnold fed 5 oz. precipitated phosphate of alumina (containing 75 per cent. of water), mixed with meat. On killing the dog, I took the spleen and liver for analysis, and separated out large quantities of alumina from them. Prof. Arnold examined the stomach, which he found congested, and also analyzed the heart, finding alumina.

It has never been asserted by me that a person eating one biscuit made with an alum baking powder, would suffer from the alumina salts present in it; but it is certain that persons continually eating biscuits made with an alum powder will suffer from its poisonous effects, as the alumina salts, instead of passing out of the system, accumulate in the various organs, interfering with their proper functions. The following experiment will show the amount of alum necessarily present in well-baked biscuits.

Sifted flour taken (1 quart)	15½ oz.
Alum baking powder (2 teaspoons)	⅝ oz.
Lard	1¼ oz.
Milk	10¾ oz.
Weight of dough	28⅛ oz.
Weight of (hot) biscuit	24¼ oz.
Loss in baking	3⅞ oz.
Weight of biscuit (cold)	23⅛ oz.
Loss on cooling	1⅛ oz.

The baking took 15 minutes. The biscuits were heavy.

Another experiment was conducted, using three teaspoons of an alum baking powder. The biscuits were quite light, showing that three teaspoons of the powder are necessary.

2 teaspoons of alum powder weighed	234 grains.
3 " " " "	351 "

The baking powder contained about 30 per cent. of burnt alum.

Therefore, there was introduced into 24¼ oz. of biscuit, 105.3 grains of burnt alum, or what is equivalent to 194.21 grains of common alum; and, as one biscuit would contain 3 grains of hydrate of alumina, a person eating four of these biscuits at a meal, would therefore introduce into his stomach 12 grains of hydrate of alumina.

IV.—Analyses of the Ashes of Certain Weeds.

By F. P. Dunnington.

With a view of obtaining some knowledge of the extent to which certain soils contain available, inorganic plant-food, I have undertaken, in the following analysis, to ascertain the comparative demands made by certain wide-spread and abundant weeds, for the main constituents of plant ashes, though, also, determining other constituents which have little bearing on the solution of this problem.

These plants were gathered just previous to flowering, each from a locality in which they were growing quite abundantly,* taking as a sample the whole previous growth of the season. Not having taken any special precautions to exclude the fine, clay dust of this locality, a small amount of alumina, iron, manganese and silica, is, no doubt, to be thus accounted for. Since some weeds are known in different localities by so different names, I give, also, the botanical names. The plants selected were the following:

1. Broom sedge (*Andropogon scoparius*), beard grass.
2. Wire grass (*Eleusine Indica*), dog's-tail grass.
3. Blue thistle (*Echium vulgare*), blue devils.
4. Potato-weed (*Solanum Carolinense*), horse nettle.
5. Purslane (*Portulaca oleracea*), pot-herb portulaca.
6. Sumach (*Rhus glabra*), common sumach.
7. Sassafras (*Sassafras officinale*).
8. Rag-weed (*Ambrosia artemesiæfolia*), bitter-weed.
9. Mullein (*Verbascum thapsus*), common mullein.
10. Dock (*Rumex obtusifolius*), broad-leaved dock.

The method adopted in these analyses was, with some few exceptions, uniform. The recently gathered plants were weighed, then allowed to slowly dry, at the common temperature, protected from dust, and re-weighed; of this, a weighed portion was heated to 110° C. until it ceased to lose weight, to determine moisture. From

* Blue thistle in flower, and not from a full patch.

20 to 50 grms of the air-dried specimens were, in small portions in porcelain crucibles, brought slowly to a low, red heat, and reduced to ashes. The impure ash was exhausted with water and then with dilute HNO_3, and the Cl determined in a fraction of this solution. The remaining portion of the ash was exposed to a red heat until all carbon was burnt off, and then exhausted with HCl and HNO_3, leaving only SiO_2 (the amount of which, when considerable, was verified by volatilization with NH_4F). The solutions obtained, united in proper proportion, were employed for the general analysis according to the usual methods. A definite fraction of this solution was treated with more than twice enough standard H_2SO_4 to unite with all the bases present, and then evaporated on the water bath until all HNO_3 and HCl were removed; the residue was then titrated with standard NaHO, thus determining the amount of acid required to neutralize the CaO, MgO, Na_2O and K_2O, not combined with the P_2O_5 and SO_3, of the ash (each molecule of P_2O_5 being precipitated in combination with two molecules of CaO or MgO). There was thus obtained, as a check on the analysis, the total relative number of molecules of the bases which had previously been weighed separately. The analyses afforded the following results, given in Table I. and Table II.:

TABLE I.—IN 100 PARTS FRESH PLANT.

	Broom Sedge.	Wire Grass.	Blue Thistle.	Potato Weed.	Purslane.
Water lost by drying in air.....	57.14	73.72	68.98	75.14	91.93
" " " at 110° C.	4.62	2.65	4.07	3.23	.96
Pure ash (excluding CO_2).....	2.24	2.45	4.69	2.17	1.52
Carbon dioxide (of ash).....	.42	.29	1.19	.47	.65
Organic matter (by difference)..	35.58	20.89	21.07	18.99	4.94
	100.00	100.00	100.00	100.00	100.00

	Sumach.	Sassafras.	Rag-weed.	Mullein.	Dock.
Water lost by drying in air.....	61.94	62.21	70.22	81.83	88.12
" " " at 110° C.	4.55	4.54	3.20	3.93	1.26
Pure ash (excluding CO_2).....	1.48	1.41	1.93	1.01	1.60
Carbon dioxide (of ash).....	.58	.39	.85	.39	.26
Organic matter (by difference)..	31.45	31.45	23.80	12.84	8.76
	100.00	100.00	100.00	100.00	100.00

TABLE II.—IN 100 PARTS PURE ASH (INCLUDING Fe_2O_3, Al_2O_3, Mn_3O_4 AND SiO_2).

	Broom Sedge.	Wire Grass.	Blue Thistle.	Potato Weed.	Purslane.
SiO_2	40.19	22.41	47.91	2.39	2.46
Cl	4.34	9.05	2.42	4.32	4.26
SO_3	2.67	12.10	2.23	11.93	3.20
P_2O_5	4.53	5.96	2.78	22.31	5.19
K_2O	31.40	34.56	16.65	23.04	60.89
Na_2O	1.23	6.09	1.41	1.19	3.52
CaO	11.50	7.34	22.44	18.40	10.67
MgO	3.45	3.81	3.49	16.47	9.47
Al_2O_3	.20	.22	.56	.11	.49
Fe_2O_3	.64	.21	.51	.55	.54
Mn_3O_4	.83	.29	.14	.26	.27
Deduct O replaced by Cl	—.98	—2.04	—.54	—.97	—.96
	100.00	100.00	100.00	100.00	100.00

	Sumach.	Sassafras.	Rag-weed.	Mullein.	Dock.
SiO_2	3.31	4.60	3.16	3.26	4.36
Cl	.81	.23	3.39	3.27	9.50
SO_3	7.94	10.89	8.00	7.32	8.27
P_2O_5	8.66	12.00	7.99	6.15	7.08
K_2O	44.18	33.36	31.40	50.12	52.67
Na_2O	2.03	6.11	.80	3.33	7.25
CaO	24.75	22.30	33.78	19.06	8.63
MgO	6.04	6.88	11.75	5.53	3.46
Al_2O_3	1.15	1.26	.00	1.15	.45
Fe_2O_3	.99	1.52	.37	1.01	.45
Mn_3O_4	.32	.91	.14	.54	.02
Deduct O replaced by Cl	—.18	—.06	—.78	—.74	—2.14
	100.00	100.00	100.00	100.00	100.00

Undoubtedly in some, if not all, of these plants, a portion of the silica is essential; but to obtain a better view of the amounts of the remaining, more important, constituents, the above results have been re-calculated, excluding the SiO_2 together with the Al_2O_3, Fe_2O_3 and Mn_3O_4, as no doubt the main portion of these latter has been derived from adherent dust.

TABLE III.—IN 100 PARTS PURE ASH (EXCLUDING Fe_2O_3, Al_2O_3, Mn_3O_4 AND SiO_2).

	Broom Sedge.	Wire Grass.	Blue Thistle.	Potato Weed.	Purslane.
Cl	7.48	11.77	4.76	4.47	4.43
SO_3	4.59	15.75	4.38	12.34	3.32
P_2O_5	7.79	7.75	5.46	23.08	5.40
K_2O	54.02	44.96	32.72	23.82	63.27
Na_2O	2.13	7.93	2.77	1.24	3.66
CaO	19.78	9.54	44.11	19.03	11.08
MgO	5.93	4.95	6.87	17.03	9.84
Deduct O replaced by Cl	—1.72	—2.65	—1.07	—1.01	—1.00
	100.00	100.00	100.00	100.00	100.00
	Sumach.	Sassafras.	Rag-weed.	Mullein.	Dock.
Cl	.85	.26	3.51	3.47	10.03
SO_3	8.43	11.89	8.31	7.78	8.73
P_2O_5	9.18	13.07	8.30	6.54	7.48
K_2O	46.90	36.37	32.59	53.30	55.60
Na_2O	2.19	6.66	.83	3.54	7.65
CaO	26.24	24.32	45.07	20.27	9.11
MgO	6.40	7.49	12.21	5.88	3.66
Deduct O replaced by Cl	—.19	—.06	—.82	—.78	—2.26
	100.00	100.00	100.00	100.00	100.00

UNIVERSITY OF VIRGINIA, Dec., 1879.

V.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN.

BY ALBERT B. PRESCOTT.

I. ALUMINATES OF POTASSIUM AND SODIUM IN SOLUTION.

The composition of certain solid aluminates of metals of the alkalies and alkaline earths, was well established long ago. Also, there are recorded observations of the action of water upon alkali aluminates, either effecting complete solution, or partial dissociation. Not finding statements of the proportions of potassium hydrate and sodium hydrate, necessary to dissolve precipitated aluminium hydrate, the writer instituted determinations of these data, in order to show the atomic ratio of K and Na, to Al, in the aluminate solutions, with different quantities of water, in the conditions of re-dissolved precipitate so common in chemical operations.*

*These operations for determination of potassium aluminate and sodium aluminate, were entrusted to the execution of Mr. J. N. Ayres.

Potassium Aluminate.

Two solutions of aluminium salt were used, one a decinormal solution of potassium aluminium sulphate, $K_2Al_2(SO_4)_4.24aq.$; the other, one-third stronger, or tenth of $1\frac{1}{3}$ normal solution of the same salt—this being a nearly saturated solution. These aluminium salt solutions were treated respectively with normal and decinormal solutions of potassium hydrate, KOH, until the precipitate at first formed had just all dissolved. The determinations were made at 30° C., then at 50°, and then at 70°; and each determination was made by triplicate trial. The three trials, accepted for each determination, did not vary one from another by as much as two-tenths cubic centimeter. The trials at the different temperatures gave the same results. When the results were attained, that the aluminium precipitate had just dissolved under the continued addition of the potassium hydrate, it was found that the addition of the first drop of decinormal solution of sulphuric acid, in all trials, reproduced the precipitate. In most cases, the quantity of aluminium salt solution taken was 5 c.c. It was the single result, under all the conditions of dilution and temperature named, that 1 *c.c. of a decinormal aluminium salt solution required* 8 *c.c. of decinormal potassium hydrate solution.* (Thus, 5 c.c. of decinormal Al_2 solution took 40 c.c. decinormal K solution, and took 5 c.c. normal K solution, and 5 c.c. tenth of $1\frac{1}{3}$ normal Al_2 solution required 53.5 c.c. of decinormal K solution, and again 5.4 c.c. of normal K solution.) This gives the proportion of potassium to aluminium, in the soluble aluminate, $K_2Al_2O_4$, or $Al_2\left\{\begin{matrix}O\\O\\(OK)_2\end{matrix}\right.$ And the equation is: $K_2Al_2(SO_4)_4 + 8KOH = K_2Al_2O_4 + 4K_2SO_4 + 4H_2O$. Calculation gives the following as the number of parts of water (*i. e.*, water solution of potassium sulphate) present for one part of the soluble potassium aluminate, in the several degrees of dilution:

With Al_2 tenth of $1\frac{1}{3}$ normal,	and K	normal,	79	parts	solution.
" " decinormal,	"	"	91	"	"
" " tenth of $1\frac{1}{3}$ normal,	"	decinor.	445	"	"
" " decinormal,	"	"	456	"	"

Over fifty years ago the compound $K_2OAl_2O_3(K_2Al_2O_4)$ was obtained by saturating potassium hydrate solution with aluminium hydrate, evaporating to a small bulk, and removing all excess of alkali by alcohol.* Fremy obtained crystals of $K_2Al_2O_4.2aq.$,

* Pogg. Annalen, **7**, 723; Gmelin's Hand-book, **3**, 320.

after fusing the alumina-saturated potash residue.* It was stated by Fremy that the di-potassium aluminate, $K_2Al_2O_4$, is decomposed by much water, precipitating aluminium hydrate, and leaving in solution an aluminate, probably $K_6Al_2O_6$. The symmetry of the compound last named, $Al_2(OK)_6$, may have had some influence in its frequent adoption, to represent the potassium hydrate solution of alumina. In nature, the form $R''Al_2O_4$ is represented by the spinels; and dibasic aluminates are formed by precipitating alkali aluminate solutions with barium or calcium hydrate solution, as is well known.

Sodium Aluminate.

Trials were made with decinormal and normal, solutions of sodium hydrate, corresponding in all particulars to the trials above-described for potassium aluminate. The results were not different in any particular. 1 c.c. of the decinormal aluminium solution, or its equivalent, gave a precipitate exactly dissolving on addition of 8 c.c. of decinormal sodium hydrate solution, or its equivalent. Therefore, the soluble sodium aluminate, in the stated conditions of dilution and temperature, is a di-sodium di-aluminium tetroxide, $Al_2\left\{\begin{matrix}O\\O\\(ONa)_2\end{matrix}\right.$ The equation will be: $K_2Al_2(SO_4)_4 + 8\,NaOH = Na_2Al_2O_4 + K_2SO_4 + 3Na_2SO_4 + 4H_2O$. The greatest dilution was 1 part of the soluble sodium aluminate in 546 parts of solution; the least dilution, 1 in about 95 parts solution.

Fremy did not obtain crystals of the sodium aluminate. Tissier† obtained four different combinations, $Na_2Al_2O_4$, $Na_6Al_4O_9$, $Na_4Al_2O_5$ and $Na_6Al_2O_6$—all in some degree soluble in water, the last-named yielding sodium hydrate to alcohol. Schaffgotsch‡ found that one molecule of aluminium oxide, fused with sodium carbonate, expels rather more than one molecule of carbon dioxide.

II. ZINC OXIDE IN ALKALINE SOLUTIONS.

In 1834, Laux§ obtained crystallized potassium zinc oxide of the symmetric composition, $K_2O.ZnO$. The crystals were soluble in cold water; but boiling water caused precipitation of $K_2O(ZnO)_2$. Fremy‖ obtained crystals of $K_2O(ZnO)_2$, these being decomposed by water.

* Ann. Chim. Phys. [3], **12**, 362 (1846); Compt. Rend., **15**, 1106.
† Compt. Rend., **48**, 627; Jahresb. d. Chem., 1859, 143.
‡ Pogg. Annalen, **43**, 117; Gmelin's Hand-book, **3**, 320.
§ Ann. der Chem. und Pharm., **9**, 165.
‖ Compt. Rend., **15**, 1106 (1846).

Ammonium zinc oxide was crystallized by Malaguti, as he reported,* with nearly the composition, $NH_3.ZnO.3H_2O$ [$NH_4OH.Zn(OH)_2.H_2O$; or $Zn(OH)(NH_2)3H_2O$]. Weyl, † by dissolving zinc in aqueous ammonia, in contact with iron, obtained the product, $(NH_3)_2ZnO$. This differs only by a molecule of water from zinc diamine, $(NH_2)_2Zn$. Neither the product of Malaguti, nor that of Weyl, appears to have been wholly soluble in water, without the help of ammonia.

I have obtained some determinations ‡ of the quantities of potassium hydrate, sodium hydrate and ammonium hydrate, respectively required to re-dissolve their precipitates in solution of zinc salt, in certain conditions of dilution and temperature. It was found that, in all conditions, some excess of the alkali needed to dissolve the precipitate, could be neutralized by an acid before the precipitate re-appeared.

At 17° C., each c.c. of a normal solution of zinc sulphate, required 8 c.c. of a normal solution of *potassium hydrate*, to re-dissolve the precipitate at first formed. (In four trials, the numbers were, of c.c., 8.0, 8.1, 8.0 and 8.0.) In taking up the excess of alkali, with semi-normal solution of sulphuric acid (each c.c. equivalent to a c.c. of the normal solution of potassium hydrate), it was found that 4 c.c. could be added before causing a precipitate. So that 4 c.c. of the KOH solution were required to retain in solution the zinc from 1 c.c. of the $ZnSO_4$ solution. The titrations with alkali and acid, then, sustain the following equations:

(1.) $ZnSO_4 + 8KOH = K_2OZnO + 4KOH + K_2SO_4 + 2H_2O.$

(2.) $K_2OZnO + 4KOH + 2H_2SO_4 = K_2OZnO + 2K_2SO_4 + 4H_2O.$

The solution with excess of alkali (not titrated back with sulphuric acid) was precipitated on adding about twelve times its volume of water. A decinormal solution of zinc sulphate required, for each 10 c.c., an average of 12.6 c.c. of normal solution of potassium hydrate, to re-dissolve the precipitate; or about fifty per cent. more, by reason of the dilution of the zinc solution from normal to decinormal. Decinormal solution of potassium hydrate would not re-dissolve the precipitate which it produced in normal solution of the zinc salt, however much was added. A solution of 16.5 grms potassium hydrate to the liter ($\frac{16.5}{56.1}$ normal) was the weakest solution that would at all re-dissolve a precipitate in the normal zinc solution. A stronger solution of potassium hydrate, 121.121 grms to the liter, was tried,

* Compt. Rend., **62**, 413 (1866).

† Jahresb. d. Chem., 1864, 165; Pogg. Ann., **123**, 353.

‡ These estimations were made by Mr. F. S. Wilson, under my direction.

and 3.8 c.c. of this, equivalent to 8.2 c.c. of normal solution, were required to dissolve the precipitate from 1 c.c. normal solution of zinc sulphate. So it appears that dilution, as far as the "normal" standard, does not lessen the solubility of the precipitate in aqueous alkali; beyond the strength of the normal solution, dilution rapidly diminishes the solubility.

The above trials were all made at 16° to 17° C. In trials at 50° C., about three times as much of the potassium hydrate solution was required to dissolve the precipitate, as at 17°, and this was true with both normal and decinormal zinc solutions. It is well known that boiling precipitates zinc from its alkali hydrate solutions.

The sodium hydrate solution was prepared from metallic sodium and adjusted to normal strength. Of this normal solution, at 17° C., 7 c.c. were needed to dissolve the precipitate made with 1 c.c. zinc sulphate normal solution. Then 3 c.c. of half-normal sulphuric acid solution were added, before a precipitate resulted. Subtracting the sodium hydrate neutralized by the acid, short of re-precipitation, we have this equation (corresponding to the result with potassium hydrate):

$$ZnSO_4 + 4NaOH = Na_2OZnO + 2Na_2SO_4 + 2H_2O.$$

The solution bears dilution with 10.5 times its volume of water before precipitation, the trial being at 17° C. At 50° C., each c.c. of the normal solution of zinc sulphate took 18 c.c., and each 10 c.c. of the decinormal zinc solution took 27.6 c.c. of the decinormal sodium solution, to re-dissolve the precipitate. It appears, then, that solution, under different conditions, requires somewhat less proportional excess of sodium hydrate than of potassium hydrate.

The normal solution of *ammonium hydrate* was adjusted in the burette, which was kept corked as much as possible. After the work, the solution was again tested, and found not to have lost strength to an appreciable extent. Each c.c. of the normal solution of zinc sulphate took 6.6 c.c. of the normal solution of ammonia. (In four trials the results were, c.c., 6.6, 6.5, 6.6, 6.6.) Of the seminormal solution of sulphuric acid, 1.6 c.c. were added, in reaching the point of precipitation. So 5 c.c. of the ammonia solution remained united with the zinc oxide and sulphuric acid of 1 c.c. of the zinc solution, indicating the equation:

$$2ZnSO_4 + 10NH_4OH = 3(NH_4)_2O2ZnO + 2(NH_4)_2SO_4 + 5H_2O.$$

The solution can be diluted with nine times its volume of water before precipitation. 10 c.c. of decinormal solution of zinc sulphate required an average of 10 c.c. of normal ammonia solution to re-

dissolve the precipitate. At 50° C., no more of the ammonia was required to re-dissolve the precipitate than at 17° C., a marked difference from the results with the fixed alkalies. It will be observed, a much smaller proportional excess of ammonium hydrate, than of potassium or sodium hydrate, is required to dissolve the precipitate.

We have, then, apparently, the following alkali-zinc oxides, intact in water solutions not too dilute:

Di-potassium zinc oxide, of a chemical identity sustained by crystalline separation: $Zn\begin{cases}OK\\OK\end{cases}$

Di-sodium zinc oxide, less certainly individualized: $Zn\begin{cases}ONa\\ONa\end{cases}$

Di-zinc-hexammonium dioxide, inferred from the constituents of its solution:

$$3(NH_4)_2O.2ZnO = \left.\begin{matrix}\\(NH_3)_6(ZnO)_2 + 3H_2O\end{matrix}\right\}$$

$$\begin{matrix}Zn—O—NH_3\\ \quad\vdots\quad NH_3\\ \quad\vdots\quad NH_3\\ \quad\vdots\quad NH_3\\ \quad\vdots\quad NH_3\\ Zn—O—NH_3\end{matrix}$$

III. SILVER-AMMONIUM OXIDE IN SOLUTION.

The proportion of ammonium hydrate required to dissolve the precipitate it first forms in silver nitrate solution, at various degrees of dilution and temperature, was carefully determined.* The results show that pretty nearly two molecules of ammonium hydrate are, in every case, required for one molecule of silver nitrate, in attaining solution of the precipitate. Conditions of dilution and temperatures do not materially influence the result. The variations in results were greater than those found with corresponding determinations for fixed alkalies, possibly owing to vaporization of ammonia, in spite of precautions. The detailed results are given below, as well as the particulars of the work. It is impossible to say how much influence is exercised by the ammonium nitrate, in dissolving the silver oxide. If this influence be disregarded, the action of the ammonia is represented by the following equation:

$$2AgNO_3 + 4NH_4OH = (NH_3Ag)_2O + 2NH_4NO_3 + 3H_2O.$$

The hypothesis of silver-ammonium oxide, $\begin{matrix}NH_3Ag\\NH_3Ag\end{matrix}\Big\}O$, is adopted as more in accord with known compounds, than the silver and ammonium oxide, NH_4AgO, or silver-ammonium hydrate, NH_3AgOH.

The solutions of silver nitrate used were the normal and decinormal. The ammonia solutions were of indefinite strength, one

* All of these determinations were carried out, with much care and discrimination, by Mr. D. E. Osborne.

near normal, and one near decinormal, and their exact strength was found after each trial, or set of trials, by titrating with solutions of oxalic acid, normal and decinormal. The burette was kept closed as far as possible, by rubber tube and pinch at the top. Five beakers were set, each with 1 c.c. of the normal solution of silver nitrate, and one beaker for titration with normal solution of oxalic acid. In the first estimation, there were required to dissolve the silver precipitate, respectively, 1.6, 1.7, 1.5, 1.6, c.c. of the nearly normal solution of ammonia, and 5 c.c. of the ammonia solution required 6.5 c.c. of normal solution of oxalic acid. Then,

$$5.0 : 6.5 : : 1.6 \text{ (average of five)} : x = 2.08.$$

In like manner, other estimations were made, mostly starting with 2 c.c. silver solution, giving results as follows:

1st	5	trials,	1 c.c.	normal	Ag	sol.	requires	2.08 c.c.	normal	NH_3 sol.
2nd	5	"	1 c.c.	"	"	"		1.95 c.c.	"	" "
3rd	5	"	1 c.c.	"	"	"		1.90 c.c.	"	" "
4th	5	"	1 c.c.	"	"	"		1.95 c.c.	"	" "
5th	5	"	1 c.c.	decinormal	"	"		2.23 c.c.	decinormal	"
6th	5	"	1 c.c.	"	"	"		2.24 c.c.	"	" "

The 1st set of trials were made at 30° C.; the 2nd, at 23° C.; the 3rd, at 24° C.; the 4th, at 23° C.; the 5th, at 30° C.; the 6th, not noted.

The silver-ammonium solutions were not precipitated by normal or decinormal solution of nitric acid, at any point of its addition; and were not precipitated by decinormal solution of sulphuric acid until the neutral reaction was reached.

VI.—Peroxide of Hydrogen and Ozone.

[First Paper.]

By Albert R. Leeds, Ph. D

Announced January 20th, 1880.

In the Chemical News (**38**, 224, 235, 243, 249 and 257) I published a series of articles, the chief object of which was to prove that when the so-called atmospheric ozonoscopes were prepared with the utmost precautions, and subjected in the laboratory, under known conditions, to the operation of vapors and gases other than ozone, such as nitrous acid, hydrogen peroxide, etc. (bodies existent to a greater or less extent in the earth's atmosphere), they all underwent change. Hydrogen peroxide affected all the ozonoscopes, thallous hydrate excepted. The results obtained with this were entered as doubtful. In one series of trials, operating with a very dilute solution of peroxide, the thallium paper was yellowed; in a second series, the yellow stain was upon the edge only of the paper, the centre remaining white. These results were there explained by the supposition of the "thallium peroxide undergoing reduction in contact with hydrogen peroxide, water and oxygen being liberated." In other words, while the effects of hydrogen peroxide in changing the thallium ozonoscope were visible, yet, accepting as true the generally received statement of Schoenbein, concerning the mutual decomposition of hydrogen and thallium peroxides, I attributed the final slight result to the reduction of any thallium peroxide first formed. This explanation was very unsatisfactory to me at the time, inasmuch as it necessitated the supposition of an initial oxidation, followed by a reduction effected by the continued operation of one and the same reagent, and I was engaged in its further study, when the publication of the admirable paper by E. Schoene, on this subject, definitely settled the question.* He there demonstrates the fallacy of Schoenbein's statement, and shows that hydrogen peroxide can convert thallous into thallic oxide, not only when the peroxide exists in solution, but also when it is in the form of vapor.

It may be regarded as established, therefore, that *none* of the so-called ozonoscopes necessarily indicate the presence of *ozone* in the atmosphere.

While my paper, written with the object of demonstrating the proposition just enunciated, was in course of publication, Mr. C. J.

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*Ann. der Chem., **196**, 58.

Kingzett made the unwarranted charge (Chem. News, **38**, 243), that I seemed "to have fallen into an error committed by many other observers, namely, that of estimating as ozone everything in the atmosphere capable of coloring so-called ozonoscope papers." Moreover, he based this charge on a misquotation, for in the paragraph he quotes, I speak, not of the ozonic reaction, but of the "so-called" ozonic reaction, an epithet which he borrows in his own article.

In a later communication (Chem. News, **40**, 96), Mr. Kingzett says, "There is no known process of slow oxidation which has been established to produce ozone." Couched, as it is, in such positive terms, this assertion contravenes the statements of those who have experimentally investigated the subject during the past forty years. It might, therefore, not unreasonably be anticipated that Mr. Kingzett should bring forward some new and crucial experiments of his own. He adduces none. At the same time, he fails to recognise certain distinguishing properties of ozone and hydrogen peroxide, and apparently is not conversant with many phenomena exhibited in the oxidation of phosphorus in moist air.

Now, the property of ozone most strikingly characteristic, is its smell. This smell, so far as long-continued familiarity with it enables me to judge, and whether the ozone is derived from the oxidation of phosphorus, or results from the action of the silent discharge on pure and dry oxygen, or accompanies the electrolysis of acidulated water (and the smell in the three cases is identical), is posesssed by ozone only. It is not the odor of phosphorus, nor of chlorine, nor of the oxides of nitrogen, although it is sometimes compared with these very dissimilar bodies. Concerning the odor of hydrogen peroxide, there appears to be wide diversity of opinion. Most of the works on chemistry, to which I have referred, state that it is odorless; one authority mentions that its odor is peculiar, another that it resembles chlorine. The solutions which I have prepared at different times myself, carbonic acid being employed to decompose the barium peroxide, have not evolved any odor that I was able to recognise or perceive. But when air is forced for a few minutes through a phosphorus ozonator, such as is described in Chem. News, **40**, 246, the atmosphere of a large lecture room becomes insupportable from the diffusion throughout it of an invisible gas (not a white smoke like the so-called antozone), and there is everywhere present the penetrating and irritating smell of ozone.

In the next place, ozone is very slightly soluble, and water through which ozone has been passed at, or below, the common temperature,

may be made to indicate the existence of dissolved ozone by appropriate tests.* It is certainly not too much to assume, that when water through which ozone has been passed, is evaporated to one-tenth of its natural bulk, its dissolved ozone is expelled. But under these circumstances, 30 c.c. of a solution which originally contained 2.7 mgrms of hydrogen peroxide, when evaporated down to 3 c.c., yielded, on titration, a result equivalent to 2.4 mgrms of the peroxide. The loss was due either to the decomposition of 0.3 mgrm of hydrogen peroxide, or to the expulsion of 0.44 mgrm of dissolved ozone. The former is by far the more probable supposition, and in either case, the body principally contained in the water was hydrogen peroxide. This water was contained in the first wash-bottle used in washing the ozone, generated by the action of phosphorus partly immersed in *aqua purissima*, upon air which had been previously purified from all pre-existent nitrogen compounds (ammonia, nitrous and nitric acids), organic particles, etc.† No *nitrous* acid was present in the water, as was shown by examination with Griess' test (metadiamidobenzole), but it contained 0.49 mgrm of nitric acid, and 0.066 mgrm of ammonia. This determination was made upon 481 liters of air, the amount of ozone found being 0.924 grm. The percentage of hydrogen peroxide in the first bottle of wash-water, as compared with the total weight of the air ozonised, was 0.00038 per cent.

In another trial, in which 420 liters of air were drawn over, and 0.805 grm ozone produced, the amount of hydrogen peroxide contained in the first bottle of wash-water, was 2.01 mgrms or 0.00037 per cent of the total weight of the air aspirated. It contained also 0.075 mgrm ammonia and 0.88 mgrm nitric acid, but of nitrous acid yielded not a trace to metadiamidobenzole. In a third experiment, in which 396.4 mgrms of ozone were produced, the wash-water contained 0.37 mgrm of nitric acid, no nitrous acid, and 1.3 mgrm of hydrogen peroxide, corresponding to 0.00039 per cent. of the total weight of the air ozonised. One word as to the close agreement in the percentages of hydrogen peroxide, found in the wash-water employed in the various trials. It was an agreement not anticipated at the outset, and became evident only when the actual amounts of hydrogen peroxide, found in the course of experiments continued during more than 3 months, came, at their conclusion, to be calculated up as percentages

*Ber. der deutsch. chem. Gesell., **12**, 1831.

†Upon Ammonium Nitrite, and Upon the By-products Obtained in the Ozonation of Air by Moist Phosphorus. JOURN. AMER. CHEM. SOC., **1**, 145. By the Author.

of the total weights of the air used. The same agreement was found to exist between the amounts of *nitric acid* present in the wash-water, when their percentages were calculated in like manner. In the first trial, 27 liters of air being aspirated, the nitric acid was 0.000318 per cent. of the total weight of the air; in the second trial, 108 liters of air aspirated, it was 0.000318 per cent.; in the fourth, 85 liters aspirated, it was 0.000303 per cent.; in the sixth, 262 liters aspirated, 0.000328 per cent. In these four experiments, water was used in the jars of the ozonator. In the third trial, 45 liters of air being drawn over, the nitric acid present in the wash-water was 0.00054 per cent; in the fifth trial, 90 liters aspirated, it was 0.00054 per cent. In these two trials, the bichromate mixture was used in the jars.

In another place,* I have shown that the amount of ozone produced by the oxidation of phosphorus, under given circumstances, is constant for any particular temperature, and consequently, the generation of ozone may be graphically represented by a curve, the production at 6° C. being nul, rising to a maximum at 24–25° C., and then rapidly diminishing as the temperature approaches 44°, the melting point of the phosphorus. The results above given, warrant, it appears to me, the formulation of another proposition, viz:

In the oxidation of phosphorus in moist air, there is formed both ozone and *hydrogen peroxide.*† The amounts of the two bodies evolved under given circumstances, bear a constant relation to one another and to the air passed over, the percentage of hydrogen peroxide being very small as compared with that of the ozone. In the experiments quoted above, the temperature being 18–21° C., the percentage of ozone, as referred to the weight of air aspirated, was 0.15 per cent.; that of the hydrogen peroxide, was 0.00038 per cent., or but one four-hundreth part of the ozone.

The amount of phosphoric acid in the wash-water, in the experiment in which 420 liters of air were aspirated, was 0.252 grm; of phosphorous acid, 0.013 grm. It was determined, by trial, that the presence of phosphorous acid in the solution, did not affect the titration of hydrogen peroxide. In this connection, it is likewise important to formulate the three following propositions:

I. No nitrous acid is present among the final products. The presence of hydrogen peroxide is, in itself, a sufficient reason.

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* Chem. News, **39**, 157.

† This statement is not new. Hydrogen peroxide was recognised by Schoenbein among the by-products of the oxidation of phosphorus.

II. Both ammonia and nitric acid are present in the final products, the amounts found, standing in a constant ratio to the quantity of air aspirated. In one trial, the results agreed with those corresponding to the formula of ammonium nitrate.

III. The generation of ammonium nitrate and hydrogen peroxide, is as invariable a feature of the phenomena observed during the course of the oxidation, as is the production of phosphoric and phosphorous acids. For this reason, any explanation of the phenomena which neglected the contemporaneous generation of ammonium nitrate and hydrogen peroxide, would be imperfect.

These results and the above conclusions, were arrived at and published in the early part of last year. The explanation brought forward at that time, and which as yet I have seen no reason to modify, was as follows:*—"As to the reason for the formation of ozone itself under these circumstances, it may be conjectured along with Lamont† and others, that it is connected with the uneven quantivalences of the elements taking part in the reaction, which may be represented by the equation: $P_4+O_{14}=P_2O_3+P_2O_5+2O_3$. If this hypothesis be true, then we should anticipate the development of ozone whenever oxidation of a perissad occurred at temperatures compatible with the stability of the ozone molecule. Even at the temperature of combustion of hydrogen, this is supposed by C. Than‡ to be the case. He explains in this manner the presence of the ozone, which he states he has detected in the combustion of hydrogenous substances generally, and its absence in the combustion of carbon.

"In entering into new combinations, the oxygen molecules must undergo temporary resolution into their constituent atoms. These, while *en route* to take up new positions in other combinations, and animated by their atomic energy, or energy of the nascent state, may either oxidize the oxygen molecule, or the nitrogen molecule, or the molecule of water. In the first place, ozone would be produced; in the second, regarding water as the basic body and NNO as the nitrile, there might be formed, as Hunt has indicated,§ ammonium nitrate; in the third, hydrogen peroxide."

Subsequent to the publication of these results, Prof. McLeod took up the subject, and arrived at the conclusion that‖ "the gas obtained

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*Journ. Amer. Chem. Soc., 1, 156.

†Chem. News, 28.

‡Journ. Chem. Soc. [2], 9, 483; Journ. pr. Chem. [2], 1, 415.

§Chemical and Geological Essays, T. S. Hunt, 2d ed., 472.

‖Chem. News, 40, 307.

during the slow oxidation of phosphorus, possesses the properties of ozone, and not those of hydroxyl, the only known peroxide of hydrogen." He likewise states that it is extremely improbable that ozone and hydrogen peroxide are both formed, as these substances destroy each other. The principal quantitative experiment mentioned, was that of passing the gas, first through a tube heated to various temperatures, then into a weighed sulphuric acid tube, and finally into a solution of potassic iodide and starch, acidified with sulphuric acid.

In connection with these experiments, it is to be noted in the first place, that Prof. McLeod regards the question in the light of an alternative, the presence of ozone excluding that of hydrogen peroxide, and *vice versa.* This view, though supported by the statements of Schoenbein,* that the two bodies mutually decompose one another, is much weakened by the recent elaborate experiments of Schoene,† who shows that when strongly ozonised oxygen, containing 5.2 volume per cent. of ozone, is agitated with a hydrogen peroxide solution containing 0.4 per cent. of the peroxide, or three to four times as much of the peroxide as is adequate to destroy all the ozone, it is only after the lapse of half an hour that as much as half of the ozone is destroyed.

Why then, if hydrogen peroxide and ozone were both present, did not a gradual increase in weight in the sulphuric acid dryer, as the gas was heated at various temperatures up to 200°, indicate the progressive decomposition of the former? The failure to obtain such a serial progression, is not explained. Neither is there any explanation of how an increase in weight in the cases where heat was applied, is necessarily to indicate the presence of hydrogen peroxide, when an increase (and that a much larger one) took place when no heat was used. Moreover, ozone itself undergoes decomposition at a temperature of 200°; but at this temperature, Prof. McLeod obtains by titration a result corresponding to 3.4 mgrms, which is relatively greater than the amount obtained when the ozone was not heated at all.

I shall be glad if Prof. McLeod will correct me of error, if I am mistaken in stating that the decomposition of his potassium iodide solution, under these circumstances, was due not to ozone (remaining after the air had been heated to 200°), but to the presence of free acid. In the early part of my own studies upon the subject, I investigated as an essential question, whether a current of ozonised air could be accurately

* Journ. f. prakt. Chem., **77**, 130.

† Ann. der Chem., **196**, 240.

titrated by an acid solution of potassium iodide, and determined that it could not.* Unless the presence of oxygen be rigorously excluded from the solution, excessively dilute acidified solutions of potassium iodide change even in the dark. In the light, the strength of the solution remaining the same, the change increases in the same ratio as the relative increase of the surface of exposure of the solution to the light's influence. But when oxygen is excluded, strong solutions containing excess of acid, may be exposed to the *direct light of the sun for days* without undergoing decomposition. Hence, when a current of air is allowed to pass through an acidified solution of potassium iodide, it is placed under conditions most favorable to its decomposition, and the amounts of iodine liberated will depend, first, upon the relative amounts of acid and iodide present; and, second, upon the intensity of the light and the relative dimensions of the surface of exposure. I have been most careful *not* to acidify the potassium iodide solution during the course of the experiment, but at its close, and then, for the reasons above-mentioned, to add only sufficient dilute acid to decompose the iodate which has been formed, and titrate at once.

In conclusion, I wish briefly to summarize the arguments above stated. The gaseous body given off in the course of the reaction between moist phosphorus and air, has a very powerful and peculiar odor, which is identical with that produced in the electrolysis of acidulated water. This is not the case with hydrogen peroxide. Ozone is very slightly soluble in water, and is readily expelled from the solution on heating. Hydrogen peroxide is miscible in all proportions with water, and solutions containing as much as one per cent. H_2O_2, may be concentrated by evaporation on the water bath, until a higher degree of concentration is reached, without great loss of peroxide (see also Schoene, Ann. der Chem., **196**, 60, and Davis, Chem. News, **39**, 221). Wash-water, through which air ozonised by phosphorus has been passed, yields, after concentration, a reaction due to hydrogen peroxide. The absence of nitrous acid in such wash-water can be readily demonstrated. No statement has been made as to the relative amounts of ozone and hydrogen peroxide *generated*, but only as to the relative amounts *evolved*. The latter amounts are those which remain after the highly dilute atmospheres of hydrogen peroxide and ozone have operated upon each other in the ozonising chamber. The absolute amounts depend upon the temperature, the period during which the ozone and hydrogen peroxide remain in con-

* Phil. Mag., April, 1879; JOURN. AMER. CHEM. SOC., 1, 18.

tact with one another, the rate of flow of gas, etc.; but under given circumstances, the ratio of the hydrogen peroxide in the *evolved* gas to the ozone is a definite quantity. In the experiments detailed, as determined upon the first portion of wash-water, it was approximately the $\frac{1}{100}$th part. It must be borne in mind, that this number does not represent the total amount of hydrogen peroxide, but only that dissolved in the first wash-bottle. This is the larger amount, but some is likewise present in the second wash-bottle, still less in the third, and so on. A portion escapes solution in the water even when a number of wash-bottles are employed, and finally passes into the potassium iodide employed to titrate the ozone. During the whole of this interval, the hydrogen peroxide and ozone are slowly decomposing one another; the results obtained, on titrating with potassium iodide solution, depending on the point in the series where the titration is effected. When the current of ozonised air issues again from the potassium iodide solution, it is laden with a white cloud. This white cloud is the antozone of Schoenbein and other authors. It is, in fact, hydrogen peroxide, held in a state of aqueous suspension, and *is the product of the action of the ozone upon the potassium iodide solution.* As such, it is to be discriminated from the white cloud, which is to be seen in the first two or three wash-bottles placed directly in connection with the ozonising chambers of the phosphorus ozonator. This latter white cloud is likewise suspended hydrogen peroxide, but its origin is to be sought for in the same series of changes as that resulting in the production of the ozone itself.

It follows, from the above, that the numbers obtained as the results of titrating the stream of ozone and hydrogen peroxide with potassium iodide, do not represent ozone only. They represent also the relatively minute amounts of hydrogen peroxide, which, as I have shown in the paper published in the early part of the preceding year, and previously alluded to, always accompany the ozone generated by the action of moist air upon phosphorus.

Finally, I desire to mention, in explanation of certain statements made in the latter part of the article, that they are founded upon experiments not as yet published, and that I have only been induced to make this preliminary notice of them, in order to complete an argument against what have appeared to me to be erroneous views.

Abstracts from American and Foreign Journals.

American Chemical Journal.

Abstractor, J. P. BATTERSHALL, PH. D.

On the Synthesis of Helicin and Phenolglucoside, ARTHUR MICHAEL (**I**, 305).

Action of acetochlorhydrose on an alcoholic solution of potassium phenate.—Acetochlorhydrose mixed with absolute alcohol, was added to an alcoholic solution of potassium phenate, the mixture allowed to stand a few hours, and the crystalline precipitate formed (potassium chloride), removed by filtration. On evaporating the filtrate, clusters of needles were obtained, which, when purified by re-crystallizatior, fused at 171–172°. This compound turns the plane of polarized light to the right, and, on treatment with dilute acids, potassium hydrate or emulsin, is decomposed into glucose and phenol. The analysis gave results corresponding to the formula $C_{12}H_{16}O_6$[$= C_6H_5(OC_6H_5)(OH_4)CHO$], and the author assigns to the new body the name *phenol-glucoside.*

Action of Acetochlorhydrose on an alcoholic solution of potassium salicylite.—The result of this reaction was the synthesis of a crystalline compound which fuses at 175–176°, has the composition $C_{13}H_{16}O_7$ [$= C_5H_6(OC_6H_4CHO)(OH)_4CHO$], and is evidently identical with helicin. It is decomposed into glucose and salicylic aldehyde by treatment with dilute acids, emulsin or hot alkaline solutions. The foregoing reactions will, it is hoped, indicate the synthesis of many of the glucosides, and assist in explaining the constitution of these compounds.

On a new formation of Stilbene, and some of its Derivatives, ARTHUR MICHAEL (**I**, 312).

Sodium acetate was allowed to act on benzoic aldehyde and phenylacetic acid, the mixture being heated in a closed tube for twelve hours. On treating the contents of the tube with hot water, a residue remains which, when purified, possesses the empirical formula of stilbene ($C_{14}H_{12}$), and coincides in its properties with this hydrocarbon. Its formation is expressed by the equation: $C_6H_5CHO + C_6H_5 - CH_2 - COOH = C_6H_5 - CH = CH - C_6H_5 + CO_2 + H_2O$. A mixture of equal parts of cumic aldehyde and phenylacetic acid, with sodium acetate, when treated in a similar manner, gave a substance which crystallizes in fine scales, fuses at 83–84°, and has the composition $C_{17}H_{18}$. To this body the author gives the name *isopropylstilbene.*

On substituting salicylic for cumic aldehyde, although the reaction does not take place in so satisfactory a manner as in the preceding case, a crystalline body was obtained, which fuses at 135–136°, has the composition $C_{14}H_{12}O$, and is probably *orthooxystilbene.*

On a New Method for the Separation and Subsequent Treatment of Precipitates in Chemical Analysis, F. A. GOOCH (**I,** 317). See this JOURNAL, **I,** 582.

On several Spanish Minerals. F. A. GENTH, JR. (**I,** 323).

Cobaltiferous gersdorffite, from Benahanis, Province of Malaga, is found associated with large, white, crystalline masses of calcite; H = 5; sp. gr. = 5.856; color, grey. The pure mineral is not affected by HCl, but is decomposed by treatment with HNO_3. The analysis gave:

S	22.01
As	39.71
Fe	1.12
Ni	24.83
Co	12.54
Cu	0.25
	100.46

corresponding to $R(SAs)_2$, in which the Ni and Co are as 2 : 1, and the S : As as 14 : 11. Associated with the gersdorffite and calcite, were found chalcopyrite, erythrite, pharmacolite, lavendulite, olivenite and arragonite.

Jamesonite, from the Province of Huelva, is massive; H = 2.5; sp. gr.=5.467; color, steel grey. It is dissolved by HCl, with evolution of H_2S, plumbic chloride separating; and by HNO_3, with separation of antimonious oxide, plumbic sulphate and sulphur. Analysis:

Fe	5.95
AgCu	0.28
Pb	38.29
Sb	33.15
S	23.60
	101.27

which, on deducting the pyrite, gives the formula: $(PbFe)_2Sb_2S_5$.

A Method for Estimating Bismuth Volumetrically, M. KUHARA (**I,** 326). Noticed elsewhere.

New Results in Electrolysis, EDGAR F. SMITH (**I,** 329). Noticed elsewhere.

Nitrosulphobenzoic Acids and some Derivatives, EDWARD HART (**I**, 340).

Metanitroparasulphobenzoic acid, $C_6H_3\begin{matrix}SO_3H\\CO_2H\\NO_2\end{matrix} + 2H_2O$, is prepared in the following manner: Toluene is dissolved in the smallest possible quantity of fuming sulphuric acid, the solution diluted, neutralized with chalk, and evaporated to a small bulk. A solution of potassium permanganate is then added, the mixture diluted, heated until it becomes colorless, filtered, and the filtrate supersaturated with hydrochloric acid. The acid barium salt of parasulphobenzoic acid is next thrown down by adding barium chloride, and from this metanitroparasulphobenzoic acid is prepared by treating it with a mixture of equal parts of fuming nitric and sulphuric acids. The Ba salt is first prepared by neutralization with basic carbonate, and the acid, by exact precipitation of the barium salt with sulphuric acid. Metanitroparasulphobenzoic acid is very soluble in water, from which it crystallizes in short prisms; in a hydrated state, it fuses at 130–131°. The Ba, Cu, Ka, Ca and Ag salts of this acid were prepared and investigated.

Metamidoparasulphobenzoic acid, $C_6H_3\begin{matrix}SO_3H\\CO_2H\\NH_2\end{matrix}$, is obtained by treating the potassium or ammonium salt of the preceding acid with an excess of ammonium sulphide, evaporating, filtering, and adding HCl. It forms warty masses, which are with difficulty soluble in boiling water. The Ba salt was made and examined. The author regards this acid as identical with that prepared by Griess from metamidobenzoic acid.

Paranitroorthosulphobenzoic acid.—The Ka salt of this acid was obtained by oxidizing the Ca salt of tolueneparanitroorthosulphonic acid with potassium permanganate. The neutral and acid Ka, and the Ca salts, were prepared.

Paramidoorthosulphobenzoic acid was made by treating the potassium salt of the above acid with ammonium sulphide, evaporating, and precipitating with HCl. It forms long delicate needles, which are slightly soluble in cold water. The Ba salt was examined.

Orthonitroparasulphobenzoic acid was prepared by treating orthonitrotoluene with fuming sulphuric acid, neutralizing with chalk, evaporating the filtrate, and oxidizing the product with potassium permanganate. The solution is then filtered, and the acid thrown down by adding HCl. The Ka and Ba salts were prepared.

Orthoamidoparasulphobenzoic acid, made from the nitro acid by treating the potassium salt with ammonium sulphide, crystallizes in rhombic plates, which dissolve in hot water. Dilute solutions of the acid show a fine blue fluorescence.

Justus Liebig's Annalen der Chemie.

Abstractor, GEO. A. PROCHAZKA, PH. D.

Constitution of Phenanthrene, GUSTAV SCHULTZ (**196**, 1–32).—Details of experiments, the outlines of which have been previously published.* Fittig and Ostermayer† obtained phenanthrenequinone on oxidation of phenanthrene, and by further oxidation, the bibasic diphenic acid; thus establishing in the hydrocarbon the bibasic C_2H_2 group. They regarded diphenic acid as a diphenylcarbon acid, though on distillation with quick-lime it did not yield diphenyl, but diphenyleneketon.‡ Graebe§ obtained diphenyl in nearly quantitative proportion, on distillation of phenanthrene with soda-lime, proving that phenanthrene, phenanthrenequinone, diphenic acid, etc., were really diphenyl derivatives. Graebe further showed that phenanthrene would form, if stilbene, dibenzyl‖ or toluol¶ were passed through incandescent tubes; the researches of Ph. Barbier,** Fittig†† and Graebe,‡‡ determined the constitution $\begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>\!CH_2$ of fluorene, the reduction product of diphenyleneketon; thus explaining the constitution of phenanthrene to the extent of $(C_6H_4)_2(CH)_2$.

Doebner§§ found that on oxidation, diparaditolyl will yield an acid distinct from diphenic acid; Carnelly‖‖ and Boernstein¶¶ proved the same in regard to orthoparaditolyl. The author*** himself has found that diphenylbenzol yields paradiphenylcarbon acid on oxidation (see also Doebner†††), entirely different from the phenylbenzoic acid obtained in the reaction of fused caustic alkali on diphenyleneketon. These results exclude the consideration of the dipara and ortho positions of the C_2H_2 group, in the question of the constitution of the phenanthrene molecule.

From the fact that diphenyleneketon is almost completely destroyed to carbon dioxide and water, on oxidation, phenylbenzoic acid completely so, A. Schmitz‡‡‡ inferred the ortho nature of phenylbenzoic acid.

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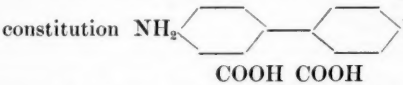
*Ber. d. d. chem. Ges., **11**, 215.
†Ibid., **5**, 936.
‡Ann. Chem., **166**, 377.
§Ber. d. d. chem. Ges., **6**, 63.
‖Ann. Chem., **167**, 131.
¶Ber. d. d. chem. Ges., **7**, 48.
Compt. Rend., **79, 1151.
††Ber. d. d. chem. Ges., **6**, 187; Ann. Chem., **193**, 134.
‡‡Ann. Chem., **174**, 194.
§§Ber. d. d. chem. Ges., **9**, 271.
‖‖Chem. Soc., 1877, 653.
¶¶Inaug. diss., Bonn, 1877. 27.
***Ber. d. d. chem. Ges., **6**, 418.
†††Ann. Chem., **172**, 115.
‡‡‡Ann. Chem., **193**, 115.

The author concludes, from the results of his experiments, that the C_2H_2 group is in diortho position in the diphenyl nucleus; that the constitution assigned to phenanthrene by Fittig and Ostermayer, is the correct one. His conclusions are based upon the following experimental data:

I. Di-iododiphenic acid, obtained from the metadiamidodiphenic acid of Griess,* by substituting iodine in place of the amido groups, yields diphenic acid on treatment with sodium amalgam.

II. The diamidodiphenic acid, obtained from dinitrodiphenic acid (m. pt., 253°), from diphenic acid, and the diamidodiphenic acid of Griess, from metaazooxybenzoic acid, are identical.

The constitution  is assigned to

the metadiamidodiphenic acid of Griess, as the barium salt on distillation with baryta (Griess), yields benzidine, the constitution of which has been determined by the author,† under the supposition that benzidine is a true derivative of the acid. On heating diamidodiphenic acid with baryta or slacked lime, a distillate is obtained, consisting largely of benzidine, but containing also another isomeric base (Struve,‡ Schultz §), which, in its pure condition, presents white needles, and melts at 157°. If soda-lime be taken, in place of slaked lime, the benzidine, formed, appears to be almost completely destroyed, the distillate containing only little benzide, consisting principally of the other base. Griess found that diamidodiphenic acid undergoes a change into an isomeric acid, when heated to 170°. The author finds that this acid does not yield benzidine on distillation with quick-lime, but only the isomeric base. Hence, the conclusion that benzidine is the true derivative of diamidodiphenic acid. The formation of the isomeric base in the above-mentioned cases is easily explained by a molecular change of part of the acid, before the lime, etc., has had opportunity to act. Griess had obtained benzidine only, having excluded the possibility of this molecular change, by distilling the barium salt with caustic baryta.

The conversion of the acid of Griess into diphenic acid, could not be effected in direct manner by sodium amalgam.

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* Ber. d. d. chem. Ges., **7**, 1609.
† Ann. Chem., **174**, 227.
‡ Ber. d. d. chem. Ges., **10**, 75.
§ Ibid., **9**, 548.

Di-iododiphenic acid $(C_6H_3)_2I_2(COOH)_2$.—By treating the nitrate of diamidodiphenic acid (suspended in water), or the aqueous solution of the hydrochloric acid salt, with nitrous acid, the difficultly soluble, corresponding tetrazodiphenic acid salts are obtained in the form of white crystals. These, on boiling with hydriodic acid, yield di-iododiphenic acid. Di-iododiphenic acid, in its pure form, is a nearly white powder, m. pt., 262°, which is readily soluble in alcohol, aceton, ether and glacial acetic acid, difficultly soluble in water. Neither the acid nor its salts could be obtained in crystals. The ammonium and sodium salts are very soluble in water; the barium salt, a light yellow powder, almost equally soluble in cold and in warm water. The mercury and silver salts are light yellow precipitates. By the action of sodium amalgam on the acid, diphenic acid was obtained.

Diamidodiphenic acid from dinitrodiphenic acid.—Hummel* found that the dinitrodiphenic acid from diphenic acid directly, and the acid obtained by Struve,† by the oxidation of dinitrophenanthrenequinone, were identical. The author confirms this result. Struve believed that the diamido acid, obtained from his dinitrodiphenic acid, and the diamidodiphenic acid of Griess, were two distinct compounds. The author, by direct comparison, establishes the identity of the two acids, as they agree in their general properties, yield the same di-iododiphenic acid, and show the same behavior on ignition with lime, baryta, etc. The memoir contains also the description of a number of preliminary experiments which had been undertaken to ascertain the constitution of phenanthrene, before the above solution was found.

Sodium and orthochlorbenzoic acid ether, when acting upon each other, did not yield the hoped for corresponding diphenic ether, but salicylic acid.

The products of the reaction of pentachloride of phosphorus upon phenanthrenequinone were not examined.

Phenanthrenecarbon acid, $C_{15}H_{10}O_2$ or $\begin{matrix} C_6H_3 \begin{cases} COOH \\ CH \end{cases} \\ | \quad \| \\ C_6H_4 \quad CH \end{matrix}$ is nearly insoluble in alcohol; easily soluble in alcohol ether; m. pt., 260°. The alkali salts are readily soluble in water. The barium salt $(C_{14}H_9COO)_2Ba + 6H_2O$, crystallizes in beautiful needles. The acid is obtained from phenanthrene nitrile, on saponification with alcoholic

* Ann. Chem., **193**, 133.

† Ber. d. d. chem. Ges., **10**, 75.

potash. On distillation of the acid with soda-lime, phenanthrene is obtained.

Phenanthrenequinonecarbon acid, $C_6H_3\begin{cases}COOH\\CO\end{cases}$ C_6H_4 CO is obtained from the former, on oxidation with chromic acid in glacial acetic acid solution.

Phenanthrenequinone, R. ANSCHUETZ and G. SCHULTZ (**32**, 57).

Crude phenanthrene materials.—1. The residues from the mother liquors obtained in considerable quantity in the course of the purification, on a large scale, of anthracene, by means of benzole (or its homologues), were subjected to fractional distillation. The fraction 310–335°, was employed. 2. The second material was purer than the former; it had been obtained as by-product in the manufacture of anthraquinone from crude anthracene, and purified by re-distillation. The fraction, 320–348°, contained about 82 per cent. of phenanthrene. Besides phenanthrene, these fractions contained anthracene (methylanthracene), fluorene, acridine, carbazol and unknown phenols.

Phrenanthrenequinone was obtained by the action of suitable mixtures of sulphuric acid, water and potassium bichromate, upon these phenanthrene materials, either with the aid of heat, or by prolonged action (1–1½ months) at ordinary temperature. The reddish-yellow crude product obtained in this manner contained phenanthrenequinone, anthraquinone (methylanthraquinone), phenanthrene, traces of carbazol, diphenyleneketon, diphenic acid, a new acid, acridine and organic chromium compounds. The last four constituents were removed by treating the material, in succession, with concentrated sulphuric acid, water, very dilute cold sodium hydrate solution, and water. The solution, which is obtained by digesting the dried residue with cold ether, contains phenanthrenequinone, anthraquinone, phenanthrene, carbazol and diphenyleneketon; the undissolved portion consists of phenanthrenequinone and anthraquinone, which could be easily separated by a slightly warmed solution of sodium bisulphite. Phenanthrenequinone alone enters into solution, and may be precipitated by a solution of potassium bichromate in dilute sulphuric acid, and purified, by re-crystallization, from tar-oils, alcohol or dilute acetic acid.

Behavior of phenanthrenequinone towards lime and solutions of the alkalies.—The author confirms the observation of Graebe in regard to the almost complete conversion of the quinone into diphenyl, on distillation with soda-lime. Soda-lime, containing considerable water, yielded fluorene, diphenyleneketon, fluorene alcohol, and a red sub-

stance. With 10 pts of quick-lime, the distillate contains diphenyleneketon principally, and fluorene. Partially slaked lime yields diphenyleneketon and diphenyl. The author attributes the reaction in the case of the wet soda-lime to the presence of water. According to the experiments of Baeyer and Friedlaender* (Caro), phenanthrenequinone is converted into diphenyleneglycollic acid, on boiling with sodic hydrate solution; according to Anschuetz and Japp,† diphenyleneketon is also produced in the reaction. The authors have found, that on prolonged boiling with potash or baryta solution, fluorene alcohol is also formed. Diphenyleneglycollic acid, on prolonged boiling with baryta solution, yields fluorene alcohol principally. The formation of fluorene would be due to the action of nascent hydrogen upon diphenyleneketon or diphenylglycollic acid.

Benzoic acid and phthalic acid both, on heating with quick-lime, yield benzole and ample quantities of diphenyl; benzamide yields water, benzole and benzonitrile.

Diphenic acid yields: 1. with quick-lime, diphenyleneketon, a red substance, and traces of diphenyl; 2. with a mixture of slacked and quick-lime, diphenyleneketon, diphenyl and a red substance; 3. with slaked lime or soda-lime, diphenyl and traces of a red body. The red substance and diphenyl were also observed on heating diphenic acid with zinc-dust.

Behavior of phenanthrenequinone towards alcoholic potash.—30 grms of phenanthrenequinone, after boiling for eight days with alcoholic potash, gave about 15 grms pure diphenic acid (compare Huyduck‡). The by-products which were obtained in the reaction were not examined.

Behavior of phenanthrenequinone towards alcoholic ammonia.—Graebe§ obtained $C_{14}H_{11}O_2N_2$ and $C_{28}H_{16}N_2$ by alcoholic or aqueous ammonia.

Phenanthrenequinone oxide $(C_6H_4)_2\begin{matrix}CNH\\|\\CO\end{matrix}$ long, yellow needles, m. pt., 167°, is easily reconverted into the quinone by concentrated hydrochloric or sulphuric acid, and subsequent dilution. It is obtained by saturating the hot alcoholic solution of phenanthrenequinone with ammonia, or adding concentrated ammonia solution to it; brown by-products, which form in considerable quantities, were not examined.

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* Ber. d. d. chem. Ges., **10**, 126, 534.

† Ibid., **11**, 211.

‡ Ann. Chem., **167**, 184.

§ Ber. d. d. chem. Ges., **7**, 785.

By digesting the ammoniacal phenanthrenequinone solution, at 100°, in closed vessels for several days, other compounds were obtained. One of these presented small, dark brown or dark green crystals, which were insoluble in the ordinary solvents, and unaffected by HCl, $SnCl_2$ or sodium bisulphite. They were soluble in concentrated sulphuric acid to a beautiful blue solution, which, after digestion on the water bath, deposited on dilution, a greenish-grey precipitate. This precipitate on sublimation yielded long, nearly colorless, needles; m. pt., 320°.

Besides the dark green body, a series of other crystallizable nitrogenous substances with basic properties had formed in the reaction, which were easily soluble in alcohol.

The behavior of the quinone towards alcoholic and aqueous potash and alcoholic ammonia, especially incline the authors to give preference to the structure $\begin{matrix}-C=O\\ |\\ -C=O\end{matrix}$ of the C_2O_2 group, in phenanthrenequinone. They acknowledge, however, that the results obtained by them do not decide this question conclusively.

Hydrogen Peroxide, EM. SCHOENE, fourth paper (**196**, 58, 74).

Hydrogen peroxide and the oxides of thallium.—Schoenbein* states that hydrogen peroxide and thallic oxide mutually reduce each other; Willm† maintains that the presence of an acid is necessary in the reaction; Weltzien‡ re-affirms the observation of Schoenbein. According to Schoenbein, thallous oxide and hydrogen peroxide do not act upon each other. From the result of a series of careful qualitative and quantitative experiments upon the action of hydrogen peroxide (aqueous solution and vapor) on thallous oxide (solution, and paper soaked in 5 per cent. thallous hydrate solution, and dried) and thallic oxide (freshly precipitated, and thallous hydrate papers which had been exposed to ozone), the author deduces as follows:

1. Thallous oxide is oxidized by hydrogen peroxide in the presence of an excess of alkali, in the same manner as the lower oxides of lead and manganese.

2. Thallic oxide is reduced in the presence of an excess of acid
$$(2H_2O_2 + T_2O_{31}H_2O + H_2So_4 = 2O_2 + T_2SO_4 + 4H_2O).$$

3. The action of thallic oxide upon neutral hydrogen peroxide is mainly catalytic; H_2O_2 is completely decomposed to H_2O and O, and

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*Journ. f. pr. Chem., **93**, 38.

†Ann. Chim. Phys. [4], **5**, 20.

‡Ann. Chem., **138**, 133.

only a small quantity of thallic oxide is reduced to thallous oxide, not sufficient to render the liquid alkaline.

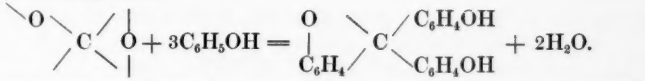
4. Thallous papers become brown in an atmosphere of hydrogen peroxide; thallic papers are not bleached, hence, the coloration of thallous papers in the atmosphere, is not conclusive for the presence of ozone in it.

Thallic oxide is slightly soluble in hydrogen peroxide solution, and is precipitated from the solution by the addition of an alkali.

Hydrogen peroxide and the peroxides of manganese and lead.*†—The behavior of these oxides towards hydrogen peroxide is the same as that of thallic oxide.

Upon Aurine,‡ R. S. DALE and C. SCHORLEMMER, second communication (**196**, 75, 91).—The body contained in commercial aurine is identical with the aurine obtained from pure phenol. The pure compound was obtained from the crude material in two ways. 1. Ammonia was conducted into the saturated spirituous solution as long as crystals continued to form. The ammonia compound was decomposed by acetic acid or hydrochloric acid, and the washed product repeatedly re-crystallized from spirits. 2. The impurities were removed by washing with cold spirits. The residue was repeatedly re-crystallized from spirits. The aurine thus obtained yields *leucaurine*, $C_{19}H_{16}O_3$, on reduction with zinc dust and acetic acid; it corresponds to the formula, $C_{19}H_{14}O_3$. The investigations of E. and O. Fisher,§ and Graebe and Caro,‖ lead to the same formula.

The authors have sought to determine the equation explaining the formation of aurine, by eliminating the complicating elements of the reaction. Pure phenol, oxalic acid and barium phenolsulphate, were heated together. The product obtained, contained impure aurine and formic acid. The slight evolution of gas consisted of equal volumes of carbonic oxide and carbon dioxide. Hence, the equation, $C_2H_2O_4 + 3C_6H_6O = C_{19}H_{14}O_3 + CH_2O_2 + 2H_2O$; oxalic acid is decomposed to formic acid, and $O=C-O-$, which enters into reaction with 3 molecules of phenol.



* Thenard, Traité de Chimie, 7 edit., Bruxelles, 1830, **1**, 209.

† Thenard, ibid,, **1**, 217; Schoenbein, Journ. pr. Chem., **75**, 96; **86**, 99; **93**, 46; Osann Chem. Centralbl., 1862, 98.

‡ Ann. Chem., **166**, 279; Graebe and Caro, ibid, 179, 184; Zulkowsky, ibid, **194**, 122.

§ Ber. d. d. chem. Ges., **11**, 195, 473, 612, 1079; Ann. Chem., **194**, 242.

‖ Ber. d. d. chem. Ges., **11**, 1116, 1348.

Ammonia aurine, $C_{19}H_{14}O_3(NH_3)_2$, obtained by saturating the concentrated spirituous aurine solution with ammonia; beautiful, dark red crystals with vivid, steel blue lustre, which lose ammonia rapidly on exposure to air, yielding aurine in the form of a reddish-brown powder.

Tetrabromaurine, $C_{19}H_{10}Br_4O_3$, small brownish-green crystals with bronze lustre, soluble in alkalies with beautiful violet color. The acidulated solutions dye silk and wool dark violet. The pure compound is obtained by adding a hot saturated, glacial acetic acid, aurine solution to a mixture of glacial acetic acid with bromine. The method applied by Graebe and Caro* in the preparation of tetrabromrosolic acid, cannot be utilized in this case.

Acetyl chloride and acetic anhydride, and aurine.—Graebe and Caro† obtained the compound, $C_{19}H_{14}O_3 + (C_2H_3O)_2O$, by the action of acetic anhydride upon aurine, at ordinary temperature or on the water bath. Small colorless plates, m. pt., 168° (Graebe and Caro, 159–160°). The pure compound may be boiled with spirits, or alcohol, without change. In the presence of a slight quantity of hydrochloric acid, the solution becomes rapidly yellow, eventually yellowish-red, and on cooling, deposits brown needles. The compound of Graebe and Caro is also produced in the reaction of acetyl chloride upon aurine, in glacial acetic acid solution. It is difficult to obtain the body pure in this manner, in consequence of the partial decomposition by the hydrochloric acid which forms in the reaction.

Compounds of aurine with acids.—$C_{19}H_{14}O_3,HCl + C_2H_4O_2$, light red, vividly glittering needles, obtained by saturating a hot glacial acetic aurine solution with hydrochloric acid gas. Even when perfectly dry, the compound possesses a strong acetic acid odor. At 110°, in a current of dry air, the acetic acid may be completely expelled; the crystals lose their lustre, and may be heated to 200° without further change.

The compound, $2C_{19}H_{14}O_3,HCl + 3C_2H_6O$, was obtained in like manner from the hot saturated, alcoholic aurine solution. At 110°, in a dry current of air, the alcohol escapes, leaving $2C_{19}H_{14}O_3,HCl$.

Similar compounds were obtained with sulphuric acid and nitric acid.

The compounds of aurine with sulphurous acid, $(C_{19}H_4O_3)_2SO_3H_2 + 4H_2O$, and the acid sulphites of the alkali metals ($C_{19}H_{14}O_3,SO_3M$), are colorless.

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*Ann. Chem., **179**, 201.

†Ber. d. d. chem. Ges., **11**, 1122.

Contribution to the Knowledge of Pyroacemic acid, CARL BOETTINGER (**196**, 92, 108).—Conclusion of the author's researches on the constitution of pyroacemic acid, the first portions of which are published in Ann. Chem., **172**, **188** and **191**.

*Destructive distillation of glyceric acid.**—Moldenhauer† states, that on distillation, glyceric acid is decomposed into carbonic acid, acetic acid, pyroacemic and pyrotartaric acids. The author has repeated the experiments of Moldenhauer, but with different results. The products obtained were gases, water, acetic acid, formic acid, an oily acid, and pyrotartaric acid. Only traces of pyroacemic acid could be detected; 1080 grms glyceric acid yielded 0.7 grm of the basic barium salt of pyroacemic acid, and 14 grms of glycuvic acid; 2 kgrms of glycerine gave 2 grms of pyrotartaric acid.

Glycuvic acid, $C_8H_{10}O_6$, m. pt., 83°, b. pt., 245–247°, shows the properties of a keton alcohol. It is freely soluble in warm water; the solution reacts very slightly acid, and deposits the substance in large, colorless leaves. The solution in dilute alcohol yields it in long, brittle needles. It is soluble in warm sodium bisulphite solution, from which it separates on cooling. If the solution, however, is heated on the water bath for some time, it will no longer deposit anything on cooling. The ammoniacal solution is not precipitated by silver nitrate. The salts, $C_8H_9KO_6$, $C_8H_9BaO_6 + H_2O$, and $C_8H_9CaO_6 + H_2O$, were obtained in translucent crystals, by concentrating the solutions of the acids neutralized with the corresponding bases. The dehydrated Ba and Ca salts, correspond to the formula $C_8H_5BaO_4$ and $C_8H_5CaO_4$. The formation of glycuvic acid from glyceric acid may be expressed by the equation: $3C_3H_6O_4 = C_8H_{10}O_6 + CO_2 + 4H_2O$.

Upon sulpholactic acid.—The author demonstrates the identity of the acid obtained by Schacht,‡ by the action of potassium sulphydrate upon α-chlorpropionic acid, and the sulpholactic acid obtained by himself from pyroacemic acid.‡ The acid melts at 141–142°; its potassium, barium and zinc salts are very soluble in water.

In the reaction of KHS on α-chlorpropionic acid, sulphodilactic acid, $C_6H_{10}SO_4$ (Schacht), was obtained in considerable quantities. The lead salt of this acid does not dissolve in water; the barium salt dissolves with difficulty in hot water. The acid yields sulpholactic acid on prolonged treatment with hydrogen sulphide.

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*Ber. d. d. chem. Ges., **10**, 266.

†Ann. Chem., **131**, 188.

‡Ann. Chem., **129**, 1; ibid, **188**, 322.

The author concludes: 1. The quantity of pyroacemic acid obtained from glyceric acid is so inconsiderable, that the formation of the acid in this manner, will offer no clue with regard to its constitutional formula. 2. The identity of the sulpholactic acid from pyroacemic acid, and from α-chlorpropionic acid, proves the ketone nature of pyroacemic acid. 3. The rational formula, $CH_3.CO.COOH$, must be assigned to pyroacemic acid.

Allyldipropylcarbinol, PAUL and ALEX. SAYTZEFF (**196**, 109, 112).—Allyldipropylcarbinol, $C_{10}H_{20}O$, a colorless liquid, insoluble in water, b. pt., 192° (769 mm), sp. gr., 0.8427, is obtained by the reaction of quantities of butyrone and allyl iodide, represented in the equation: $(C_3H_7)_2CO + C_3H_5I + Zn = (C_3H_7)_2.C_5H_3.CO(Zn)$. The reaction product contains diallyl, unaltered butyrone and the carbinol. The actual yield of the carbinol was 30 per cent. of the theoretical.

The acetic acid ester boils at 210° (751 mm); sp. gr., 0.8733. The carbinol combines with 2Br; on oxidation with chromic acid it yields carbonic acid, butyrone, formic, butyric and propionic acids, and an inconsiderable quantity of a non-volatile acid.

Allyldiethylcarbinol, AL. SCHIROKOFF and AL. SAYTZEFF (**196**, 113, 116).—$C_8H_{16}O$, colorless mobile liquid, b. pt., 156°, is obtained by the reaction of allyl iodide, diethylketone and zinc. By the action of bichromate and sulphuric acid, there were obtained diethylketone, acetic acid, propionic acid, and a small quantity of another acid, which was not examined.

Action of Tertiary Butyl Iodide upon Isobutylene in the Presence of Metallic Oxides, J. LERMONTOFF (**196**, 116, 122).—Tertiary butyl iodide was saturated with isobutylene at 10°, the mixture filled into tubes containing twice the quantity of CaO requisite for the absorption of the total iodine. The tubes were sealed, and maintained at a temperature of 100° for twenty hours. Two products were obtained: *Isodibutylene*, identical with the compound obtained by Butlerow, by the action of sulphuric acid upon isobutylene or trimethylcarbinol, and *isotributylene.* The reaction may be expressed by the equations:

$$C_4H_8 + C_4H_9I - HI = C_8H_{16};$$
$$C_8H_{16} + C_4H_9I - HI = C_{12}H_{24}.$$

The same isotributylene was obtained by the action of tertiary butyl iodide on isodibutylene, in the presence of lime.

Trimethylethylene and its Derivatives, and the Chemical Structure of Pinakon, D. PAWLOW (**196**, 122, 128).—The author finds that tetramethylethyleneglycol, derived from tetramethylethyl-

ene, and the pinakone, obtained from acetone by the action of sodium amalgam, are identical.

Dimethylisopropylcarbinol boils at 117° (744 mm); m. pt., — 14°; sp. gr., 0.8232.—Tetramethylethylene is obtained from the iodide of this carbinol, by the action of alcoholic potash solution. The pure compound is a colorless liquid which is insoluble in water; b. pt., 73° (760 mm). The bromide dissolves in ether, from which it crystallizes in long needles. The chlorohydrate is obtained by the action of fuming hydrochloric acid on the hydrocarbon, at ordinary temperature; colorless, oily liquid, which becomes solid in the cold, b. pt., 112°. The hydroiodic compound boils at 140°, and solidifies on cooling. The chemical structure of the hydrocarbon appears from the manner of its preparation, but was further verified by its behavior on oxidation, when it yields acetone only. The hydrocarbon is easily polymerised on treatment with sulphuric acid.

The glycol was prepared from the bromide. 70 grms of the hydrocarbon gave a yield of about 7 grms of the pure glycol. The crystallized product, as obtained from the aqueous solution, melts at 46.3°, and corresponds in all its properties to pinakon hydrate, $C_6H_{14}O_2$. $6H_2O$, from acetone.

Nicotine and Nicotinic acid, R. LAIBLIN (**196**, 129, 182).

Preparation of nicotine.—The aqueous tobacco extract, after concentration, was distilled with lime, the distillate slightly acidulated with a known quantity of oxalic acid, and then concentrated to the consistency of a thin syrup. This extract was decomposed by concentrated caustic potash solution, corresponding in quantity to the oxalic acid previously employed. The oily crude nicotine thus obtained, was distilled in a current of hydrogen, the distillate dissolved in ether, and precipitated by oxalic acid. The precipitate was decomposed, as before, by concentrated potash, and the base obtained, subjected to a careful fractional distillation in a slow current of hydrogen. The fraction, 240–242°, represents pure nicotine. The odor of the pure alkaloid is peculiarly narcotic, differing from that of tobacco. One hundred pounds of air-dried tobacco yielded about 600 grms of the pure product (1.2 p. c).

Nicotinic acid, $C_6H_5NO_2$ (pyridinecarbon acid, C_5H_4NCOOH), is obtained in the form of the potash salt, on oxidation of aqueous nicotine solution, by means of potassium permanganate, under precautions in regard to which reference must be had to the original. The acid is identical with the pyridinecarbon acid ($C_6H_5NO_2$) obtained by Huber*

* Ann. Chem., **141**, 271; Ber. d. d. chem. Ges., **3**, 849.

on oxidation with chromic acid mixture, and the nicotinic acid obtained by Weidel,* on oxidation with HNO_3, to which he has assigned the formula, $C_{10}H_8N_2O_3$. The acid was prepared from the silver salt by treatment with H_2S. It is also obtained on decomposing chlorohydronicotinic acid chloride by water, separation of HCl and nicotinic acid by fractional precipitation with $AgNO_3$; decomposition of the silver by H_2S. Colorless needles; m. pt., 225–227°.

Silver salt, $C_6H_4AgNO_2$, difficultly soluble in water, voluminous, white precipitate or long, thin, colorless needles, $(C_6H_4NO_2)_2Ca + 5H_2O$, very difficultly soluble in water; very easily yields supersaturated aqueous solutions. The aqueous solution, on spontaneous evaporation, yields it in very large crystals. $C_6H_4KNO_2$, small colorless, fatty scales, extremely deliquescent. Platinum double compound, $(C_6H_5NO_2)_2 2HClPtCl_4 + 2H_2O$, very large, dark orange, well developed crystals (or long thin needles), obtained on the addition of concentrated $PtCl_4$ solution to a solution of nicotinic acid in hydrochloric acid. $(C_6H_5NO_2)_2 2HClAuCl_3$, small, yellow scales. Hydrochloric acid compound, $(C_6H_5NO_2)HCl$, is obtained from the solution of nicotinic acid in dilute hydrochloric acid, on spontaneous evaporation, in small crystals or frequently in very large plates. $C_6H_5NO_2HBr$.

The *lime salt, on distillation with lime*, yields pyridine principally, hydrogen, (dipyridine), inconsiderable quantities of ammonia, carbonic oxide and hydrocarbons; methylamine does not form. This reaction identifies nicotinic acid as pyridinecarbon acid. The author recommends the pure lime salt as a suitable source for the preparation of pure pyridine.

Chlorohydronicotinic acid chloride.—A body, which appears to correspond to the formula $C_5H_4NCOCl + HCl$, white soluble needles, was obtained by the action of pentachloride of phosphorus on potassium nicotinate. The compound is very easily decomposed. The yield was small.

Ethyl ether of nicotinic acid, is obtained in combination with HCl (as $C_5H_4NCO_2C_2H_5 + HCl$), a crystalline compound, by the action of alcohol on chlorohydronicotinic acid chloride. On the addition of sodic hydrate to the aqueous solution, the ether separates in oily drops; it has very little permanence, and could not be obtained in a pure condition.

An attempted synthesis of nicotinic acid by the action of chlorocarbonic acid ether on pyridine, proved unsuccessful. The products

* Ann. Chem., 165, 328.

obtained were ethyl chloride, neutral carbonic acid ether and hydrochloride of pyridine.

Distillation of nicotine salt with lime.—The salt employed was $C_{10}H_{14}N_2 + 2HCl + ZnCl_2 + 4H_2O$ (H. Vohl*). The products obtained were: pyrrol, C_4H_5N, ammonia, methylamine, a solid base ($C_{10}H_{11}N$?), large quantities of hydrogen, traces of saturated and non-saturated hydrocarbons. The chloride of the solid base ($C_{10}H_{11}N$?), yields a characteristic carmine colored precipitate with $PtCl_4$, which is easily soluble in warm dilute alcohol, or dilute sulphuric acid to beautifully dark red solutions.

Upon the Nature of Cohesion and its Chemical Signification, FRIEDR. MOHR (**196**, 183, 213).—Not suitable for abstraction.

Chloranilines and Chlornitranilines, F. BEILSTEIN and A. KURBATOW (**196**, 214, 238).

Dichloranilines.—The theory admits of six different dichloranilines. Three of these were known. The other three were obtained by the author, either by reduction of corresponding nitrodichlorbenzoles, or by chlorination of monochloranilines.

1. *p–dichloraniline*, $C_6H_3NH_2.Cl_2Cl_5$ (Jungfleisch †; Lesimple ‡), long, thick needles (from ligroin solution), which are readily soluble in alcohol, ether, and CS_2; difficultly soluble in ligroin, very difficultly in water. *Acetyl derivative*, $C_6H_3Cl_2NH(C_2H_3O)$. The authors recommend in the preparation of acetyl derivatives, gradual addition of chloracetyl to the mixture of equivalent quantities of the base and glacial acetic acid, the reaction to be terminated with the aid of heat, the reaction product to be poured in water, and re-crystallized from 50 per cent. acetic acid. Dichloracetanilide, small needles, which are insoluble in CS_2 and ligroin, very difficultly in cold benzole, difficultly in 50 per cent. acetic acid, and easily in alcohol; m. pt., 132°. p–dichloraniline yields on chlorination *trichloraniline*, $C_6H_2NH_2ClClCl$(1. 2. 4. 5); on nitration, $C_6H_2NH_2ClNO_2Cl$ (1. 2. 4. 5) and $C_6H_2NH_2ClClNO_2$ (1. 2. 5. 6)(?).

2. *Unsymmetrical or (a)–o–dichloraniline*, $C_6H_3NH_2ClCl$ (1. 3. 4.), long, broad, glistening needles, which are difficultly soluble in ligroin; m. pt., 71.5°; b. pt., 272°. *Acetyl derivative*, small needles, pretty soluble in 50 per cent. acetic acid; m.pt., 120.5°. On chlorination, it yields the two trichloranilines, $C_6H_2NH_2Cl_3$ (1.3.4.6 and 1.2.3.4); on nitration, $C_6H_2NH_2Cl_2NO_2$ (1.3.4.6) and $C_6H_4NH_2NO_2Cl_2$ (1.2.[?]3.4).

* Journ. pr. Chem. [2], **2**, 331.

† Ann. Chim. Phys. [4], **15**, 252.

‡ Zeitschr. f. Chem., 1868, 226.

3. *Adjacent* or (*v*)–o–dichloraniline (1.2.3), needles which are easily soluble in alcohol, difficultly in ligroin; m. pt., 23–24°; b. pt., 252°. *Acetyl derivative* needles (from benzole solution), pretty difficultly soluble in benzole, or 50 per cent. acetic acid, very difficultly in ether or ligroin, more easily in alcohol.

4. (*a*)–*m–dichloraniline* (1.2.4.) (Authors,* Witt†); m. pt., 63°; b. pt., 245°. *Acetyl derivative;* m. pt., 143°.

5. *Symmetrical or* (*s*)–*m–dichloraniline* (1.3.5) (Witt‡); m. pt., 50.5°; b. pt., 259–260° (740.6 mm). *Acetyl derivative*, m. pt., 186–187°.

6. (*v*)–*m–dichloraniline* (1.2.6), is obtained in needles, from dilute alcohol; easily soluble in ligroin, or strong alcohol; m. pt., 39°. *Acetyl derivative*, needles, easily soluble in alcohol, or 50 per cent. acetic acid; m. pt., 175°.

Dichloranilines are obtained on chlorination of chloranilines, as follows: 1. p–chloraniline yields exclusively (*a*)–m–dichloraniline. 2. o–chloraniline yields exclusively (*a*)–m–dichloraniline. 3. m–chloraniline yields p–dichloraniline and (*a*)–o–dichloraniline.

Nitrodichloranilines: (*s*)*–nitro–p–dichloraniline*, NH_2ClNO_2Cl (1.2.4.5), yellow needles, easily soluble in alcohol and CS_2, pretty difficultly in 50 per cent. acetic acid, almost insoluble in ligroin; m. pt., 153°. *Acetyl derivative*, difficultly soluble in 50 per cent. acetic acid. It is obtained on nitration of p–dichloracetanilide. 2. *v–nitro–p–dichloraniline*, $NH_2ClClNO_2$ (1.2.5.6.), is obtained besides the former on nitration of p–dichloraniline. It appears to be identical with the reaction product of ammonia upon β–dinitro–p–dichlorbenzole (Koerner). Light yellow needles; m. pt., 67–68°. *Acetyl derivative;* m. pt., 204–205°. 3. (*s*)*–nitro–*(*a*)*–o–dichloraniline*, $NH_2ClClNO_2$ (1.3.4.6), is obtained on nitration of (*a*)–o–dichloraniline, or on heating nitrotrichlorbenzole, Cl_3NO_2 (1.3.4.6) with ammonia; m. pt., 175°. Acetyl derivative; m. pt., 123–124°. 4. (*v*)*–nitro–*(*a*)*–o–dichloraniline*, NH_2NO_2ClCl (1.2.3.4[?]), forms on nitration of (*a*)–o–dichloraniline; m. pt., 95–96°. *Acetyl derivative;* m. pt., 152–153°. 5. (*v*)*–nitro–*(*v*)*–o–dichloraniline*, $NH_2ClClNO_2$ (1.2.3.6), is obtained on heating (*v*)–nitro–v–trichlorbenzole with ammonia; m. pt., 162–163°. 6. *p–nitro–*(*s*)*–m–dichloraniline*, NH_2ClNO_2Cl (1.3.4.5), forms on nitration of (*s*)–m–dichloraniline; m. pt., 170–171°. Acetyl derivative, 222°. 7. o–nitro–(*s*)–m–dichloraniline, $NH_2NO_2Cl_2$ (1.2.3.5), is also obtained on nitration of (*s*)–m–dichloraniline; m. pt., 79°. Acetyl derivative; m.

* Ann. Chem., **182**, 95.

† Ber. d. d. chem. Ges., **7**, 160.

‡ Ber. d. d. chem. Ges., **8**, 145.

pt., 138–139°. 8. o–nitro–(a)–m–dichloraniline, $NH_2Cl_2NO_2$ (1.2.4.6), is obtained on nitration of dichloracetanilide; m. pt., 100°. Acetyl derivative; m. pt., 188°. 9. p–nitro–(*v*)–m–dichloraniline, NH_2ClNO_2Cl (1.2.4.6), forms on chlorination of p–nitroaniline; m. pt., 188°. Acetyl derivative; m. pt., 210°.

Trichoranilines: 1. (*s*)–trichloraniline, $C_6H_2NH_2Cl_3$ (1.2.4.6) (Hoffmann,* Mills†), was obtained by chlorination of acetanilide. Long, soft needles, soluble in ether, alcohol, CS_2, etc.; m. pt., 77.5; b. pt., 262°. *Acetyl derivative*, needles obtained by the action of chloracetyl on trichloraniline at 100° in sealed tubes. Very little soluble in ether, ligroin, CS_2, more easily in 50 per cent. acetic acid or alcohol; m. pt., 204°. 2. (*s*)–a–trichloraniline, NH_2Cl_3 (1.2.4.5) (Lesimple‡), was obtained by chlorination of p–, (*a*)–o dichloraniline and (v)–m–monochloraniline. Thick needles; m. pt., 95–96°. Acetyl derivative; m. pt., 184–185°. 3. v–trichloraniline, NH_2Cl_3 (1.2.3.4), is obtained besides the former on chlorination of (*a*)–o–dichloraniline, and m–chloraniline, and on reduction of nitro–v–trichlorbenzole; m. pt., 67.5°; b. pt., 292°. Acetyl derivative; m. pt., 120–122°.

Nitrotrichloraniline: $C_6HNO_2NH_2Cl_3$ (1.2.3.4.6[?]). Nitrotrichloracetanilide was obtained by nitrification of a–trichloraniline. Colorless needles; m. pt., 193°. By digestion of the anilide in sealed tubes at 100°, precipitation by water and re-crystallization from alcohol, the pure *nitrotrichloraniline* was obtained in yellow needles; m. pt., 124°. 2. A nitro derivative could not be obtained from (*s*)–trichloracetanilide.

Tetrachloranilines: 1. a-tetrachloraniline, NH_2Cl_4 (1.2.3.4.6), was obtained by chlorination of a mixture of isomeric dichloranilines; m. pt., 88°. *Acetyl derivative*, needles, m. pt., 173–174°. It is not decomposed on distillation with caustic soda solution. 2. v–tetrachloraniline (1.2.3.4.5) was obtained by reduction of nitro–(*v*)–tetrachlorbenzole by means of tin and hydrochloric acid; m. pt., 118°. 3. s–tetrachloraniline (1.2.3.5.6) (Lesimple §).

Hydrogen Peroxide, fifth paper, Em. Schoene (**196**, 239–258). —1. *Behavior towards ozone* (Schoenbein‖; Meissner¶; C. Hoffman** Engler and Nasse ††; Brodie ‡‡). The result reached by the author

* Ann. Chem., **53**, 35.
† Ann. Chem., **176**, 355.
‡ Ann. Chem., **137**, 125.
§ Zeitschr. f. Phys., 1868.
‖ Journ. pr. Chem., **77**, 130, 143, 264.
¶ Unterschungen ueber den Sauerstoff, Hanover, 1863, 256.
** Pogg. Ann., **132**, 617.
†† Ann. Chem., **154**, 222.
‡‡ Philos. Transact., **162**, 2, 435.

with regard to neutral hydrogen peroxide solution, coincides with what Brodie has shown of the alkaline solution. 1. In the neutral decomposition of ozone and hydrogen, both lose equal volumes of oxygen. 2. The gas containing the ozone expands by a volume equalling the sum of the oxygen volumes lost by the two bodies.

With regard to the behavior of ozone towards water, the author remarks: 1. The quantity of ozone in a dry gas is very considerably decreased when it comes in contact with water. 2. After the gas has come with water, and if it remains in contact with water, the quantity of ozone decreases only slowly (in the course of 3 days the quantity of ozone had decreased one-half; after 15 days, only traces of ozone remained). 3. In the conversion of moist ozone to ordinary oxygen (at ordinary temperature), its volume expands in the ratio of 2 : 3.

Behavior towards chlorine (Brodie,* Aschoff†). The quantity of oxygen evolved is equal to the quantity contained in the hydrogen peroxide. The reaction may be explained by the equations $H_2O_2 + Cl_2 = 2HCl + O_2$ (Brodie, Weltzien‡), or $H_2O[O+O]H_2 + Cl_2 = H_2O + O_2 + 2HCl$.

Upon Camphor Chlorides, F. V. SPITZER, part first (**196**, 259, 264). Gerhardt,§ in a brief notice, states that on the reaction of PCl_5 upon camphor, $POCl_3$ and $C_{10}H_{16}Cl_2$, are formed, which latter compound yields, on distillation, an oil, presumably $C_{10}H_{15}Cl$. According to Pfaundler,‖ the product varies according to the quantity of PCl_5 employed, being either $C_{10}H_{16}Cl_2$, or $C_{10}H_{15}Cl$. The author has instituted a series of experiments with varied proportions of camphor, and PCl_5, without as yet having been able to obtain $C_{10}H_{15}Cl$, the existence of which compound seems to him questionable (see also Montgolfier ¶). Only dichlorides seem to form in the reaction. Two isomeric dichlorides were identified; one of these melts at 87.5–90°, the other crystallizes in feathery needles, dissolves easily in ether, and melts at 155–155.5°.

Upon some Sulphur Oxychlorides, F. CLAUSNIZER (**196**, 265, 298).

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* Philos. Transact., **2**, 800; Proc. Roy. Soc., **11**, 442; Ann. Chim. Phys. [3], **65**, 506; Journ. Chem. Soc. [2], **1**, 326.

† Journ. pr. Chem., **81**, 487.

‡ Ann. Chem., **115**, 127, 138, 141.

§ Lehrbuch, **3**, 775.

‖ Ann. Chem., **115**, 29.

¶ Compt. Rend., **85**, 286.

Suphurselenium oxychloride.—H. Rose assigned the formula $2(SeCl_6,5SO_3),5(SeCl_4,SeO_2)$ to the product obtained by him in the reaction of sulphuric anhydride upon selenium tetrachloride. Berzelius has already conjectured that it was SO_3SeCl_4, contaminated with sulphuric acid. The sulphurselenium oxychloride was obtained by the author in a variety of different ways. 1. The reaction upon each other of $SeCl_4$ (1 mol.) and $SO_2Cl(OH)$ (2 mol.) begins in the cold, but must be terminated with the aid of heat. The mass, on cooling, solidifies to a crystalline cake, which, after drying on porous clay plates over sulphuric acid, yields the pure $ClSO_2—O—SeCl_3$. 2. Sulphuryl chloride (1 mol.) and selenium oxychloride (1 mol.), at ordinary temperature, yield $SeCl_4$, apparently according to the equation $SO_2Cl_2 + SeOCl_2 = SO_3 + SeCl_4$. If the mixture, however, is heated to 170–180°, in sealed tubes for several hours, SO_3SeCl_4, is obtained. 3. Pyrosulphuric acid (1 mol.) and $SeCl_4$ (1 mol.), when heated together, yield SO_3SeCl_4 ($S_2O_7H_2 + SeCl_4 = SO_3SeCl_4 + SO_4H_2$). Towards the end of the reaction a slight evolution of HCl becomes noticeable. This method of preparation is recommended as being the least expensive and troublesome. 4. Sulphuric acid, SO_4H_2, when acting upon $SeCl_4$, also yields sulphurselenium oxytetrachloride. The equation, $3SeCl_4 + 2SO_4H_2 = SO_2 + 2SO_3SeCl_4 + 4HCl$, rep. esents the principal reaction. The reactions, $SeCl_4 + 2SO_4H_2 = SOCl_2 + S_2O_7H_2 + 2HCl$, and $SeOCl_2 + 2SO_4H_2 = SeO_2 + S_2O_7H_2 + 2HCl$, take place in a minor degree. 5. Pyrosulphuryl chloride and selenium tetrachloride react upon each other according to the equation, $Se_2O_5Cl_2 + SeCl_4 = SO_3SeCl_4 + SO_3 + Cl_2$. 6. Sulphurylhydroxylchloride and selenious oxychloride, when acting upon each other, lead to SO_3SeCl_4. The reaction takes place in the two stages, $2SO_2Cl(OH) + SeOCl_2 = SeCl_4 + S_2O_7H_2$; $SeCl_4 + S_2O_7H_2 = SO_3SeCl_4 + SO_4H_2$. 7. Sulphurylhydroxylchloride and selenious anhydride react upon each other, when heated: $2SO_2Cl(OH) + SO_2 = S_2O_7H_2 + SeOCl_2$; $2SO_2Cl(OH) + SeOCl_2 = S_2O_7H_2 + SeCl_4$; $S_2O_7H_2 + SeCl_4 = SO_3SeCl_4 + SO_4H_2$. Sulphurselenium oxytetrachloride crystallizes in white needles; m. pt., 165°; b. pt., 183° (Rose 187°); the dry substance is decomposed at once, on exposure to air; it is violently decomposed when brought in contact with water. The vapor density determination at 209°, gave d=3.362 (calculated 10.426). Dissociation evidently takes place: $2SO_3SeCl_4 = 2SO_3 + S_2Cl_2 + 3Cl_2$; the products of dissociation combine again, on cooling, to the original substance. The author contrasts the properties of $SeSO_3Cl_4$ and $S_2O_3Cl_4$. $S_2O_3Cl_4$ forms only in the cold, and is slowly decomposed at ordinary temperatures, rapidly at the m. pt. (57°),

the products being $S_2O_5Cl_2$, SO_2Cl_2, Cl_2 or SO_2Cl_2 and $SOCl_2$. $SSeO_3Cl^2$ requires the aid of heat in its formation, and is not decomposed at ordinary temperatures, in sunlight, or on heating. $S_2O_3Cl_4$, with little water, yields SO_2, HCl, $SOCl_2$ and $S_2O_5Cl_2$ or $SO_2(OH)Cl$. $SeSO_3Cl_4$, with water, undergoes the same decomposition as a mixture of SO_3 and $SeCl_4$, yielding H_2SO_4, $SeOCl_2$ and SeO_2, and finally H_2SeO_3. Concentrated sulphuric acid (H_2SO_4) acts violently upon $S_2O_3Cl_4$: $S_2O_3Cl_4 + 2SO_4H_2 = 3SO_2Cl(OH) + SO_2 + HCl$ (Michaelis); while it does not act at all upon $SeSO_3Cl_4$ in the cold, and very slightly on heating: $SSeO_3Cl_4 + 3H_2SO_4 = 2S_2O_7H + SeOCl_2 + 2HCl$ and $SeOCl_2 + 2SO_4H_2 = S_2O_7 + SeO_2 + 2HCl$. These differences would be further proofs for the theorem of Michaelis, which states: "that the affinity of selenium to chlorine is considerably greater than to oxygen, the affinities of N and O to Se are smaller, the affinities of Cl greater than the affinities of these bodies to sulphur." The author adduces a further proof in the behavior of SeO_2 towards Se_2Cl_2. $2SeO_2 + 2S_2Cl_2 = 2SeOCl_2 + SO_2 + S_3$; $2SeOCl_2 + S_2Cl_2 = Se_2Cl_2 + 2SOCl_2$; $SOCl_2 + SeOCl_2 = SO_2 + SeCl_4$ (Michaelis).

Sulphurylhydroxylchloride.—The author finds the b. pt., at 150–151° (726 mm). *Selenium tetrachloride,* vapor density found, 3.922 (calc. 7.63); dissociation evidently according to the equation $2SeCl_4 = Se_2Cl_2 + 3Cl_2$. *Selenious anhydride,* sp. gr. = 3.9538. *Selenious acid,* sp. gr. = 3.0066. *Selenium oxychloride* was obtained by heating $SeCl_4$ (1 mol.) and SeO_2 (1 mol.), in sealed tubes to 200° for several hours; b. pt., 175–176° (753 mm). *Sulphuryl chloride* is decomposed on prolonged boiling, yielding $SO_4H_2SO_2$ and Cl_2. The pure compound boils at 72–73°, and is decomposed only slowly in contact with water at ordinary temperature.

Sulphurtitanium oxytetrachloride.—$ClSO_2 — O — TCl_3$, was obtained in the form of a white powder, in the reaction of $SO_2(OH)Cl$ upon $TiCl_4$.

The corresponding *antimony* compounds could not be obtained by the action of $SO_2(OH)Cl$, either upon $SbCl_3$ or $SbCl_5$; neither was it possible to obtain the corresponding *tin* or *silicium* compounds in like manner from $SnCl_4$ or $SiCl_4$.

The author attempted in various ways to reach the bromides corresponding to $SO_2(OH)Cl$ or $S_2O_3Cl_4$, but unsuccessfully.

The Coloring Matters and Glycoside Sugar of Persian Berries, C. LIEBERMANN and O. HOERMANN (**196,** 299, 338).—

The statements of different authors (Henry,* Kane,† Binswanger and Winkler,‡ Gellatly,§ Persoz,‖ Orthel,¶ Hlasiwetz,** Bolley,††Schuetzenberger,‡‡ Schuetzenberger and Bestèche,§§ Lefort,‖‖ Stein¶¶) in regard to the coloring matters and glycoside sugar, vary considerably.

The authors sum up their own results as follows:

1. The berries, positively those of *Rhamnus infectorius* and *tinctoria*, contain, even after many years, about 12 per cent. coloring matter glycosides, besides little free coloring matter. 2. The glycoside, dissolving more difficultly in spirits, is identical with Kane's xanthorhamnin, and corresponds to the formula $C_{48}H_{66}O_{29}$. The more soluble glycoside, Schuetzenberger's β–rhamnegin, does not appear sufficiently established. 3. Xanthorhamnin does not undergo a molecular change by acids, as stated by Lefort, but is decomposed into rhamnetin and isodulcit, the latter being the same sugar as results from quercitrin. Isodulcit is also contained in the more soluble glycoside. 4. Rhamnetin corresponds to the formula $C_{12}H_8O_3(OH)_2$, first assigned to it by Schuetzenberger, and appears in a large number of its derivatives. 5. Xanthorhamnin and rhamnetin are not identical with quercitrin and quercetin. 6. Aqueous berry decoctions deposit a coloring matter, not originally pre-formed in the berries, Lefort's rhamnin, a glycoside which is formed by the action of a ferment on one of the glycosides. It is not, as stated by Lefort, identical with xanthorhamnin, but probably has not yet been obtained in pure condition.

Xanthorhamnin was obtained in solution, by digesting the coarsely powdered berries for ten hours with boiling 85 per cent. alcohol. The pure compound presents microscopic needles of beautiful gold color; dissolves very easily in water, easily in alcohol, but is insoluble in ether, benzole, or chloroform. The air-dried substance crystallized from alcohol, contains crystal-alcohol ($C_{48}H_{66}O_{29} + 2C_2H_6O$). Xanthorhamnin dissolves in alkalies without decomposition. Sugar of lead solution colors the solution orange; a beautiful orange-colored precipitate is produced on addition of ammonia. Silver nitrate yields

* Journ. pr. Chem., **26**, 226.
† Phil. Mag., **23**, 3.
‡ Jahresber., 1849, 488.
§ Edinb. New Phil. Journ., **7**, 252.
‖ Traité sur l'Impression des Tissues, **1**, 547.
¶ Bull. Soc. Ind. Mulh., **30**, 16.
** Ann. Chem., **112**, 107.
†† Ibid, **115**, 54.
‡‡ Ann. Chem. Phys. [4], **15**, 118.
§§ Bull. Soc. Ind. Mulh., **35**, 456.
‖‖ Compt. Rend., **63**, 840, 1081; **67**, 343.
¶¶ Journ. pr. Chem., **105**, 97; **106**, 1.

a silver mirror. Fe_2Cl_6 colors xanthorhamnin solution dark brown. Fehling's solution colors green, and is reduced on application of heat. The potassium salt, $C_{48}H_{62}O_{29}K_4$, is very easily soluble in water, difficultly in alcohol, and very little permanent when moist.

Xanthorhamnin, by prolonged drying at 130°, is partially decomposed into sugar and rhamnetin. Yeast does not produce fermentation in xanthorhamnin solutions.

Rhamnetin.—Dilute sulphuric acid does not act upon aqueous xanthorhamnin solution in the cold; on heating, the liquid becomes turbid and suddenly deposits a clean, intensely lemon-colored, precipitate of rhamnetin. If the application of heat is interrupted before the separation of the precipitate is perfected, the complete separation takes place slowly in microscopic crystals. Rhamnetin dissolves very little in boiling water and the ordinary solvents. Warm phenol dissolves it in considerable quantity, and yields it in crystals on cooling. The color and dyeing capacity of rhamnetin is more intense than of xanthorhamnin. Rhamnetin dissolves readily in ammonia, alkalies and alkaline carbonates. The alcohol solution yields precipitates with alum water, copper acetate, lead acetate. Fehling's solution is reduced on heating; silver nitrate, at ordinary temperature. Alumina mordant is dyed canary color; iron mordant, black.

Dimethylrhamnetin, $C_{12}H_8O_5(CH_3)_2$, is obtained on digestion of xanthorhamnin potassium, dehydrated potassa, methyl sulphate and absolute methyl acohol, at 120°. Light yellowish needles; m. pt., 156–157°, insoluble in water and dilute alkalies, soluble in alcohol. *Acetylrhamnetin*, $C_{12}H_8O_3(OC_2H_3O)_2$, was obtained by boiling equal weights of rhamnetin and anhydrous sodium acetate with 3 to 4 parts of acetic anhydride. Acetic anhydride and sodium acetate combine to $CH_3-C(OC_2H_3O)(OC_2H_3O)(ONa)$ which, in consequence of its tendency to yield normal acetate, causes the acetylisation according to the equation

$$CH_3-C(OC_2H_3O)(OC_2H_3O)(ONa) + X(OH)(OH) = X(OC_2H_3O)(OC_2H_3O) + CH_3-COH(ONa) (=$$

$CH_3CO_2Na + H_2O$).

Beautiful, white silken needles, which are easily soluble in glacial acetic acid, less so in alcohol; m. pt., 183–185°.

Propionylrhamnetin, $C_{12}H_8O_5(C_3H_5O)_2$, colorless needles; m. pt., 158–162°. *Benzoylrhamnetin*, $C_{12}H_8O_3(OC_7H_3O)_2$, obtained in the reaction of benzoic anhydride and rhamnetin, colorless silken needles; m. pt., 210–212°. *Dibromrhamnetin*, $C_{12}H_8Br_2O_5$, yellow needles, easily

soluble in warm alcohol and glacial acetic acid. *Dibromacetylrhamnetin*, colorless needles; m. pt., 211–212°.

Isodulcit.—A re-examination of the isodulcit from quercitrin proves that it does not crystallize in the forms of cane sugar (Reuss), but clinorhombic crystals (Hirschwald). The decomposition of xanthorhamnin is represented by the equation: $C_{48}H_{66}O_{29} + 5H_2O = 2C_{12}H_{10}O_5 + 4C_6H_{14}O_6$.

Azophenols, P. Weselsky and R. Benedikt (**196**, 339, 349).—The azophenols were obtained by the action of melting potassium hydrate on mononitrophenol. *Paraazophenol* prepared from paranitrophenol (m. pt., 114°), forms beautiful, light-brown crystals, without metallic lustre; m. pt., about 204°; partial decomposition at this temperature. Formula of the air-dried substance, $C_{12}H_{10}N_2O_2 + H_2O$; the crystal water escapes at 100°. The compound dissolves easily in alcohol, ether, or benzole, very difficultly in water. *Salts:* The salts of the alkalies yield beautifully orange-colored solutions. $C_{12}H_8BaN_2O_2 + 4H_2O$, yellow crystals, was obtained by the addition of aqueous baryta solution to the alcoholic azophenol solution. *Tetrabromparaazophenol*, $C_{12}H_6Br_4N_2O_2$, gold-colored needles. Paraazophenol was also obtained by the action of paradiazophenol nitrate upon phenol potassium ($HOC_6H_4 — N_2NO_3 + KOC_6H_5 = HOC_6H_4N = NC_6H_4OH + KNO_3$).

Orthoazophenol crystallizes without water of crystallization, in gold colored scales; m. pt., 171°. The sublimed azophenol forms beautiful reddish-yellow needles. It is insoluble in water, difficultly soluble in cold alcohol; ether dissolves it easily. The *barium* salt crystallizes in beautiful red needles. *Tetrabromorthoazophenol*, dark yellow needles, with metallic lustre.

Metaazophenol could not be obtained by fuming metanitrophenol with potash.

Action of Water upon the Haloid Compounds of the Alcohol Radicals, second paper, Gustav Niederist (**196**, 349, 360).—The results of the author confirm the supposition expressed by him,* that the haloid compounds of mono-valent and bi-valent alcohol radicals may be nearly always converted into alcohol, on treatment with an excess of water. *Methyl iodide* could be easily converted into *methylic alcohol, iodide of allyl* into *allyl alcohol.* The author recommends the latter reaction for the preparation of pure allyl alcohol. *Hexylene* and *hexylic* alcohol were obtained by heating *hexyl iodide* (from mannite) with water (100°). *Benzyl chloride*, at 100–110°,

* Ann. Chem., **180**, 388.

gave about 76 per cent. of the theoretical quantity of *benzyl alcohol*, and other products which were not examined.

Haloid compounds of the olefines. Preparation of ethyleneglycol. 60.5 per cent. of the theoretical quantity of ethyleneglycol was obtained by heating ethylenebromide for 130 hours, with 26 parts of water in champagne bottles, in the water bath.

Propyleneglycol. By boiling propylenebromide with an excess of water, *propyleneglycol* (b. pt., 186°) and *acetone* were obtained. The reactions are represented in the equations:

$$CH_3 - CHBr - CH_2Br + 2H_2O = CH_3CHOH - CH_2OH + 2HBr, \text{ and}$$

$$CH_3 - CHBr - CH_2Br + H_2O = CH_3 - CO - CH_3 + 2HBr.$$

Amylene bromide (from commercial amylic alcohol), after 30 hours boiling with an excess of water, had been completely decomposed. The only product obtained (b. pt., 94–96°), appears to be amylene oxide.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office**, by ARNO BEHR.

January 6, 1880.

223,212.—*Galvanic battery.* ROBERT C. ANDERSON.

223,265.—*Electro-plating with nickel.* JOSEPH WHARTON.

Brief: This improvement consists in the substitution for the nickel anodes now in use, which are usually of the cast metal, rarely pure and often alloyed, of an anode of wrought or rolled malleable nickel.

223,363.—*Manufacture of printing ink.* JULIUS KIRCHER.

Suitable for cancelling ink and postal stamps. For method of using and composition, the specification must be seen.

January 13, 1880.

223,442.—*Preparing a sizing material used by paper-makers.* ROB'T A. FISHER.

A solution of sulphate of alumina is treated with oxide of zinc.

223,443.—*Manufacture of a white compound for paper-makers' use.* ROB'T A. FISHER.

The ferric sulphate contained in impure sulphate of alumina is first reduced to ferrous sulphate, and then the solution treated with oxide of zinc, as in the preceding patent.

223,459.—*Sizing for paper.* GEORGE VINING.

The sizing consists of caseine, or a mixture of caseine and borax.

223,463.—*Method of preparing an aqueous bleaching solution of soda or potassa.* PETER T. AUSTEN.

Claim: A bleaching solution composed of silicates of sodium or potassium, barium peroxide, and the hydrates of sodium, potassium or ammonium.

223,558.—*Apparatus for aging liquors.* JOSEPH C. VETTER.

Effects the aging by means of galvanic currents through the liquid, for which purpose a special apparatus is constructed.

223,571.—*Manufacture of anhydrous sulphuric acid.* JOHANN A. W. WOLTERS.

Sulphuric anhydride is prepared by heating a mixture of pyrosulphate of sodium and sulphate of magnesium. The residue is a double salt of sulphate of sodium and magnesium, which can be separated into its component parts by crystallization and used again in the process.

223,602.—*Treatment of hops for preservation.* LOUIS NAUMANN and CARL POHL.

The hops are moistened with alcohol and compressed into suitable receptacles.

223,608.—*Apparatus for drying and deodorizing liquid manures.* ADALBERT BARON VON PODEWILS.

January 20, 1880.

223,735.—*Manufacture of artificial stone or marble.* WM. H. HOOPES.

223,738.—*Process of tempering steel.* JOSEPH C. JENKINS.

Application of yellow prussiate of potassium, nitrate of potash and cyanide of potassium.

223,747.—*Apparatus for refining camphor.* WM. V. MCKENZIE.

223,762.—*Preparation of gelatine for vitrifiable prints.* EMILE SALVY.

January 27, 1880.

223,814.—*Preparing paper and other fabrics and materials for wrapping silver and other metals to prevent them from tarnishing.* JOHN C. PENNINGTON.

The paper is impregnated with a solution of oxide of zinc or lead, in caustic soda potassa or ammonia.

223,815.—*Manufacture of cement and artificial stone.* FREDERICK RANSOME.

223,860.—*Electro-deposition of nickel.* JOSEPH H. POTTS.

Claims a solution for nickel-plating, composed of acid solution of nickel sulphate to which carbonate of lime has been added.

223,880.—*Composition for elastic rollers.* JAMES BURBRIDGE, ROBERT C THORPE and THOMAS OAKLEY.

Consists of "sulphurized oil," fibrous material and gum, resin or pitch.

223,913.—*Extracting metals from ores.* OTTOKAR HOFMANN.

A process of successive treatment with chlorine and washing, for the particulars of which, the specifications must be seen.

Foreign Patents.

Condensed from R. BIEDERMANN'S Report to the German Chemical Society by OTTO H. KRAUSE.

F. W. DUPRÉ and C. N. HAKE, Stassfurt: *Manufacture of potassium sulphate from schoenite.* (Germ. P., No. 8021, Jan. 21, 1879.)—100 parts of finely ground schoenite ($K_2SO_4MgSO_4,6H_2O$), are mixed, dry, with 14 parts of slaked or unslaked lime. The water of crystallization of the schoenite suffices for the decomposition of the mixture into calcium sulphate, potassium sulphate and magnesia. The plastic mass is either calcined or allowed to remain at rest for several days, whereupon it is ready for lixiviation.

G. LOEWIG, Dresden, and F. LOEWIG, Goldschmieden: *Process of purifying alumina which has been used for clarifying liquids, &c.* (Germ. P., No. 6713, Oct. 13, 1878.)— Spent colloid alumina is mixed, in equivalent proportions, with lime, evaporated, and heated to destroy organic matter. The calcium aluminate is re-dissolved, and the alumina precipitated. Or, the spent alumina is evaporated and heated with hydrochloric acid or magnesium chloride, to destroy organic matter. The aluminum chloride or magnesium aluminate formed, are treated in known manner to obtain aluminum hydrate.

AD. HERRAN, Paris, and A. CHAUDÉ, Terres: *Method of obtaining coloring matters by the action of nitrobenzole or nitrotoluole upon mixtures of aniline or its homologues and metallic double chlorides.* (Germ. P., No. 7991, Dec. 28, 1878.)—The inventors employ, among others, the following double chlorides: Aluminium-magnesium chloride, aluminium-zinc chloride, aluminium-ferrous chloride, ferro-magnesium chloride, ferri-zinc chloride.

A red, and a grey, coloring matter may be obtained by heating 2 parts of toluidine with 1–1½ parts double chloride, and addition of 1½ parts nitrobenzole, or 1½ parts nitrotoluole, until the mass becomes viscid. The red is soluble in boiling water, and the grey coloring matter is rendered soluble in water after conversion into the sulpho-acid.

A blue coloring matter is obtained when a mixture of 2 parts aniline and 1–1½ parts aluminium-zinc chloride, is heated to near the boiling point of aniline, 1–1½ parts of nitrobenzole added, and the heating continued for several hours. The mass is dissolved in concentrated sulphuric acid, the coloring matter precipitated by water, and dissolved in alkali.

MEISTER, LUCIUS and BRUENING, Hoechst: *Method of preparing coloring matters by the action of chlorinated quinones upon secondary and tertiary aromatic amines.* (Germ. P., No. 8251, June 24, 1879.)—I. Violet dyes are obtained by allowing

crude chloranil, prepared by Graebe's method (Ann. d. Chem. u. Pharm., **146**, 1), to react upon mono- and di-methylated bases of the benzole series. For instance, 1 part of chloranil is added gradually to 2 parts of dimethylaniline, and the mixture kept at 60–70° C. for some time.

II. Blue coloring matters: 2 parts of methyldiphenylamine and 1 part of chloranil are heated upon the water bath until the mass becomes viscous. It is then further heated at 120–130° C., until a sample of it may be pulverized upon cooling.

III. Green coloring matters are produced by the action of chloranil upon benzylated diphenylamine and its homologues. 3 parts of benzyldiphenylamine are heated to 60° C. upon the water bath, 1 part of chloranil stirred in gradually, and the mass kept at 60–80° C., until it becomes brittle upon cooling.

A. ZELTNER, Nuremberg: *Preparation of ultramarine red from ultramarine violet.* (Germ. P., No. 8327, Aug. 14, 1878.)—Violet ultramarine is exposed in thin layers to the action of hydrochloric acid in a vessel or chamber of brick. Heat is applied to the outside, and the temperature kept at 130° until the violet ultramarine is converted into the red.

A. REIBECK, Halle on Saale: *Manufacture of illuminating gas.* (Germ. P., No. 8455, July 25, 1879.)—Sawdust, saturated with gas oil, is spread between two layers of coal upon a charging tray, and placed in the retort.

C. KURTZ, Cologne: *Improvements in the manufacture of nitro-glycerine.* (Germ. P., No. 8463, May 22, 1879, being an addition to Germ. P., No. 6208; see this JOURNAL, **1**, 404.)—Glycerine, in a sort of emulsion obtained by blowing cold compressed air into it, is put into the acid mixture. By passing a current of cold air into the vessel in which the reaction takes place, the temperature of its contents can be regulated.

The nitro-glycerine is syphoned off, washed with water and alkali, and purified by fractional crystallization, whilst cooled air is being passed through it.

W. LESEMEISTER, Cologne: *Apparatus for the preservation of beer.* (Germ. P., No. 8331, Mar. 25, 1879.)—Beer is heated to 100° C., in a copper kettle, to destroy ferments, and pumped through a cooling arrangement to a reservoir in which suspended matters, particles of yeast, etc., are allowed to subside. The beer is then re-impregnated with the carbonic acid lost during the heating.

O. BOURGAN, Schoeningen: *Purification of feed water for boilers, by means of barium sulphide.* (Germ. P., No. 8492, Mar. 25, 1879.)—Barium sulphide carefully dissolved in hot water, is employed. The sulphuric acid is completely precipitated, the barium sulphate carrying down with it calcium carbonate, and evolving hydrogen sulphide. Any carbonic acid or calcium bicarbonate still present, is removed with milk of lime. By this means, the formation of magnesium or ammonium chloride in waters containing magnesium, sulphate or ammonical salts, is avoided, an advantage over de Haen's chloride of barium process.

J. A. SIEGLITZ & CO., Leipsic: *Method of dyeing furs brown, and leaving the tips of the hairs white.* (Germ. P., No. 6095, Dec. 1, 1878.)—As a reserve for the tips of the hairs, a paste composed of 10 parts gum arabic, 5 parts acetate of lead, 10 parts soft unctuous clay and 10 parts basic acetate of copper, is applied. Oxide of lead dissolved in milk of lime, dyes the hair brown, by forming sulphide of lead with the sulphur contained in the hair, or with ammonium sulphide subsequently added. The reserve is then washed out.

BENRATH and FRANCK, Gelbe Muehle, near Dueren: *Gelatinized tracing paper.* (Germ. P., No. 5881, Nov. 26, 1878.)—Tracing paper is passed between rollers through a weak solution of glue, pressed, and dried without the aid of steam.

W. KELBE, Carlsruhe: *Method of purifying rosin oil.* (Germ. P., No. 7369, Oct. 9, 1878.)—"Rosin oil," obtained by the dry distillation of colophony, containing about 20 per cent. of undecomposed rosin, and possessing a disagreeable smell of wood-tar, besides exhibiting a blue fluorescence, is purified as follows:

The crude oil is heated to 120° C., in a vessel provided with a stirring apparatus and but partially filled by the oil. 8 liters of soda lye, sp. gr., 1.215, are then added per 100 lbs. of oil, and the contents of the vessel kept slowly boiling during half an hour, the evaporating water being continually replaced. After this heating, 50 liters of water per 100 lbs. oil are stirred in, and the whole kept at a temperature of 50–60° C., which must be carefully maintained. Solution of sodium chloride or excess of soda lye, precipitates rosin soap. After the oil and the lye have separated as much as possible, the latter is drawn off, and the oil subjected to two washings, with 25 liters of warm water each time. It is turbid from suspended water, smells strongly, and still fluoresces. To divest it of these properties, it is exposed to the air for several days, in shallow iron vessels, at a temperature of 60–80° C. The water and the more volatile oils evaporate, whilst the substance which causes the fluorescence disappears.

The soap lye and wash waters are collected in tanks, and impregnated with carbonic acid. The rosin which is thereby separated in clots, may again be subjected to dry distillation, the same as fresh rosin.

J. W. KLINGHAMMER, Brunswick: *Preparation of saccharate of lime from syrup, using a minimum of lime.* (Germ. P., No. 8311, Jan. 19, 1879.)—To the syrup, heated to 100° C., only so much caustic lime in powder is added, as is necessary to form calcium saccharate.

Indifferent substances, such as pulverized marl or brick, sawdust, sand, &c., are added to absorb the solutions of the salts contained in the syrup, as well as the potassium saccharate.

FRED. HARRY MOST, Widnes: *Cover for packages or drums, which are to contain caustic soda or similar substances.* (Engl. P., No. 5052, Dec. 10, 1878.)—The under side of the cover is provided with bent projections, or bars, which become imbedded in the caustic soda as it cools.

A. RUEMPLER, Hecklingen: *Preparation of magnesia, free from iron and calcium sulphate, from crude magnesium chloride.* (Germ. P., No. 8777, June 15, 1879.—The inventor proposes to use the last liquors of the manufacture of potash salts from carnallite, containing besides magnesium chloride, considerable quantities of magnesium sulphate. Iron is first removed from the liquor, by adding one-fifth per cent. of its weight of caustic lime. The magnesium sulphate is converted into magnesium chloride and calcium sulphate, by the addition of calcium chloride. From the clarified liquor, magnesia is precipitated by calcium hydrate.

In a similar manner, magnesia may be obtained from kieserite or epsom salts, by previously precipitating with calcium chloride, a solution from which ferric oxide has been removed by a small addition of calcium hydrate.

JEAN PIERRE SERVE, Givors: *Manufacture of phosphorus.* (Engl. P., No. 49, Jan., 1879.)—A blast furnace with closed top, is charged alternately with coke or

coal, and mixtures of coal, quarz or acid silicates, with earthy phosphates (apatite, coprolites, bones). These mixtures are formed into bricks. The products of combustion, carbonic oxide and phosphorus vapor, pass through a lateral opening, into a cooling apparatus composed of a number of pipes surrounded by water. (The method of decomposing calcium phosphate, by heating with silicic acid and coal, was proposed by Woehler. It was worked in the same manner as described in the above patent, by Brisson; see Wagner's Jahresber. 1870, 200. It will probably be found difficult to prevent the blast from burning the phosphorus.—Note of R. Biedermann.)

ALFRED HENRY ALLEN, Sheffield : *Treatment of gases containing sulphurous acid.* (Engl. P., No. 189, Jan. 16, 1879.)—Gases obtained in the roasting of ores, &c., are freed from flue dust and moisture, and pass into an absorption apparatus filled with charcoal. The pores of the latter absorb the sulphurous acid, and allow all, or nearly all, the nitrogen to escape. The charcoal is prepared by heating it to redness, and cooling it in an atmosphere of nitrogen. The absorbed sulphurous acid can be withdrawn from the charcoal, by heating it to 300–400° C., or by connecting the apparatus with an air pump, or both.

CARL JULIUS STEUER, Blasewitz: *Artificial stone from quartz-sand and plumbic oxide.* (Germ. P., No. 8011, April 9, 1879.)—Ground quartz-sand is mixed with 2–10 per cent. of finely ground plumbic oxide, the whole slightly moistened with sodium silicate, again well mixed, and then pressed into the desired form. It is dried at a low temperature, and subsequently fired.

FRANC. LAUR, Paris : *Improvements in the manufacture of aluminium sulphate.* (Eng. P., No. 173, Jan. 15, 1879.)—The contents of this patent are chiefly a reproduction of Eng. P., No. 771, Feb. 25, 1878; see this JOURNAL, 1, 406 and 458. Besides the use of zinc, it is recommended to apply an electric current.

HENRY WASS MERRITT, Somerville, and W. HORNBY IRELAND, Boston, Mass: *Carburation of gas and air.* (Eng. P., No. 152, Jan. 14, 1879.)—The carburetting apparatus, protected from variations of temperature, contains a fibrous material saturated with hydro-carbons, through which the gas is made to pass. The inventors actually propose to pass the carburetted gas through a solution of mercuric nitrate, in order to remove acetylene, to which they ascribe very pernicious qualities.

FRANZ STROEHMER, Kotschenbroda, and THEODORE SCHLOZ, Dresden : *Apparatus for withdrawing gases from coke ovens, combined with an automatic pressure regulator.* (Germ. P., No. 8174, May 29. 1879.)—To prevent the valuable products formed in coking, ammonia, tar oil, carbon bisulphide, &c., from being decomposed by coming in contact with the heated walls of the furnace, iron pipes are run down to near the level of the coal. The products of the distillation are drawn off through lateral pipes. These pipes are provided with an automatic regulator, to avoid damage to the quality of the coke, by exhausting too rapidly.

ADOLF, COUNT BUONACORSI DI PISTOJA, Vienna, LOUISA STEFFEN, Vienna, and JOSEF DRUCKER, Bruenn : *Extraction of sugar from syrup, by the substitution process.* (Germ. P., No. 8346, June 26, 1878.)—Syrup containing about 50 per cent. of sugar, is diluted with 6 times its weight of water, and 28 parts of lime per 100 parts of sugar, added at a temperature of 0–15° C. This solution is heated to 110° C., when tricalcium saccharate ($C_{12}H_{22}O_{11},3CaO$) precipitates, and is

filtered off hot. To the cooled filtrate, as much syrup and lime are added as will bring the amount of sugar and lime to the percentage present in the initial solution. This operation is repeated 20 to 25 times, whereupon lime only is added to the filtrates, in order to separate the sugar from the accumulated impurities.

MISCELLANEOUS.

Prize Question

CONCERNING THE ACTION OF PHOSPHORIC ACID FERTILIZERS.

From Biedermann's Centralblatt fuer Agricultur Chemie.

Translated by Bruno Terne, Ph D.

An association of German manufacturers of fertilizers, has resolved to offer a prize of 1500 reichsmarks for the best, and 500 reichsmarks for the second best, solution of the following question, viz.:

To prove by numerous experiments, made under varying conditions, in pots, parcels of field and meadow land, and with due regard to previous experiments, the influence that phosphoric acid manures, with and without additions of potash and nitrogen, exert on the value of fodder plants (clover, grass, lupines, etc.), namely, on the increase of albuminous matter, starch, sugar and fat therein. It is also desirable, for the purpose of comparison, to include the *reverted* phosphoric acid, or the phosphate of lime soluble in citrate of ammonia, in the experiments.

The undersigned has, at the request of the association, consented to act as prize-juror, in conjunction with Prof. Dr. T. Nessler, of Carlsruhe, and Prof. Dr. G. Kuehn, of Moeckern.

Papers for competition must be sent in before April 1st, 1881, sealed and signed with a motto. There should also be affixed, thereto, a sealed envelope containing the motto in question, and the name of the author.

Prof. Dr. F. Nolte,
Editor of the "Landw. Versuchsstationen."

Tharandt, *December*, 1879.

The names of the firms belonging to the above-mentioned association, are:

H. & E. Albert, Bieberich, a. Rh.
Michel & Co., Ludwigshafen.
Mueller, Packard & Co., Wetzlar.
Vorster, Grueneberg, Kalk.
J. C. Zimmer, Mannheim.
Fertilizing Co., Kaiserslauten.

THE AMERICAN CHEMICAL SOCIETY.

VII.—Proceedings.

Meeting, February 5th, 1880.

Fourteen members present. This not being a quorum, no regular business was transacted, but Prof A. R. Leeds read a paper (informally) upon "Peroxide of Hydrogen," and Mr. Jas. H. Stebbins made some remarks about the action of acids upon certain coloring matters. After which, meeting adjourned.

ARTHUR H. ELLIOTT,
Recording Secretary.

VIII.— Analysis of a Mineral resembling Thorite.

By Peter Collier, Ph.D.

Chemist to the Department of Agriculture, Washington, D. C.

This mineral was said to be taken from the Champlain iron region, but the exact locality is not known to the writer. In most of its physical properties it resembles thorite, or orangeite, but a carefully executed analysis showed it to differ from them in containing considerably more uranium oxide.

The following are some of its properties: *color*, dark red-brown; *lustre*, resinous, or sub-vitreous; *streak*, yellow-brown; *fracture*, sub-conchoidal; *hardness*, about 5, scratches glass with difficulty, but is easily scratched by the knife; *specific gravity*, 4.1265; *fusibility*, infusible in very fine fragments in the blow-pipe flame; *in closed tube*, gives considerable water, residue red-brown; *on charcoal*, heated alone, becomes brown, no fumes. With sodic carbonate, forms a dark grayish-brown bead. No reduced metal. *Salt of phosphorus*, on platinum wire, in both oxidizing and reducing flames, gives a yellowish color while hot, and a light green when cold. *Borax*, on platinum wire, in both oxidizing and reducing flames, gives a yellow bead while hot, and pale amber when cold. In both beads, considerable matter was undissolved.

A preliminary analysis was made, taking 1.328 grms of the finely powdered mineral, a quantity found to be too large for very accurate work, because of the difficulty of washing the bulky precipitates.

The final analysis was made, taking .5387 grm, and is believed to be correct, because each residue weighed was proven true to name, and pure. The absence of cerium, lanthanum, didymium, and zirconium, was proven. The following is a brief description of the method of analysis:

1. Decomposed with hydrochloric acid, evaporated to strict dryness, and silica separated by filtration.

2. Precipitated lead in the filtrate by sulphuretted hydrogen. The scanty, black precipitate was treated in a crucible, with nitric and sulphuric acids, thus converting the lead to sulphate, in which form it was weighed.

3. The filtrate was precipitated by ammonic sulphide, in presence of ammonic chloride and excess of ammonic hydrate. After washing the black precipitate thoroughly with water containing ammonic sulphide, it was dissolved in hydrochloric acid, evaporated until nearly free from acid, and treated with a concentrated solution of potassic sulphate. The precipitated potassic-thoric sulphate was washed with solution of potassic sulphate dissolved in boiling water, and precipitated, in the first analysis, by sodic hyposulphite, and in the second analysis, by ammonic hydrate. After ignition, this precipitate was weighed as thoric oxide; it had a light yellowish color, not due to iron oxide.

The filtrate from potassic-thoric sulphate was precipitated black, by ammonic sulphide and hydrate, and thus freed from excess of potassic sulphate. After solution of the precipitate in hydrochloric acid, the iron and aluminium oxides were precipitated as basic acetates, and separated from each other in the wet way by potassic hydrate.

The filtrate from the basic acetates was precipitated by ammonic sulphide and hydrate, thus getting rid of the sodic acetate, which prevents complete precipitation of uranium as hydrate.

The black uranium sulphide was dissolved in hydrochloric acid, and precipitated as hydrate by ammonic hydrate. After ignition, in a covered crucible, the precipitate was weighed as uranoso-uranic oxide (U_3O_4), from which was calculated the amount of uranic oxide (U_2O_3). This residue was entirely free from iron and manganese oxides.

4. Lime, magnesia, and alkalies, were determined in the usual manner.

In view of the homogeneous structure of this mineral, its similarity to thorite, and its marked excess of one important constituent (uranium), the name "URANO-THORITE," is suggested as appropriate.

The analyses were made by one of my assistants, Mr. Henry B. Parsons.

ANALYSES OF URANO-THORITE.

	PRELIMINARY.	FINAL.
Moisture and combined water		11.31
Silica, SiO_2	19.43	19.38
Thoric oxide, ThO	52.51	52.07
Lead oxide, PbO	.40	.40*
Aluminic oxide, Al_2O_3		.33
Ferric oxide, Fe_2O_3		4.01
Uranic oxide, U_2O_3		9.96
Calcic oxide, CaO		2.34
Magnesic oxide, MgO		.04
Sodic oxide, Na_2O		.11
		99.95

April 15th, 1880.

IX.—Development of Sugar in the Sorghums.

By Peter Collier, Ph.D.

During the season of 1879, a series of examinations were conducted upon four varieties of sorghum, for the purpose of learning more about the development of sugar in these plants, and, if possible, of reconciling the conflicting testimony, which has accumulated during the past twenty-five years, since their first introduction into this country.

The results obtained are prospectively of such immense practical importance, that apart from their scientific bearings, it seems that none can but feel a lively interest in them.

The four varieties of sorghum experimented upon, were known as the Early Amber, the White Liberian or Goose-neck, the Chinese or Sumac, and the Honduras or Mastodon.

The seed was planted in the grounds of the Department of Agriculture, at Washington, D. C., on or about the 15th of May, and the culture was in all respects like that of Indian corn.

When the flower head first appeared, the examinations began, and these examinations were continued at intervals of from 5 to 7 days during the season.

For each examination, two or three stalks of each variety were selected, their development, length, weight, &c., noted down. After

* From preliminary analysis.

stripping off the blades, the stalks were equally divided into butts and tops, the juice expressed from each, and its specific gravity, content of sucrose (crystallizable sugar), glucose (uncrystallizable sugar), and total solid matter, carefully determined. Besides these determinations, the water present in the fresh, unpressed stalks was also determined.

The glucose was determined by Fehling's solution, and the sucrose, after inversion, in like manner, and there appeared to be no trouble in securing results of considerable accuracy, as evidenced by repeated tests in duplicate. The polarization of the juice was also taken in every case.

The first examinations of the Early Amber and of the White Liberian varieties, were made July 18th, and through the season these two varieties, although quite unlike in appearance, showed a marked resemblance in their development.

The examinations of the Chinese began August 6th, and those of the Honduras, August 12th. The examinations were concluded upon the 8th of November.

The first examinations of these four varieties gave the following results:

July 18th, Early Amber, 3.77 per cent. glucose and 4.43 per cent. sucrose, in juice from entire stalks.

July 18th, White Liberian, 4.1 per cent. glucose and 5.7 per cent. sucrose, in juice.

August 6th, Chinese, 5.55 per cent. glucose and 1.85 per cent. sucrose, in juice.

August 12th, Honduras, 5.13 per cent. glucose and 1.2 per cent. sucrose, in juice.

The above results represent the percentage of glucose and of sucrose, in the juice from both butts and tops.

Successive examinations showed, in every case, a rapid increase in the amount of sucrose and a decrease in the amount of glucose present in the juice, although the increase of the former was far greater than the decrease of the latter, as will be evident by the following results of examinations made at later periods in the development of the plants.

August 13th, the Early Amber gave 1.74 per cent. glucose and 14.25 per cent. sucrose.

August 13th, the White Liberian gave 2.0 per cent. glucose and 13.8 per cent. of sucrose.

September 13th, the Chinese gave 1.45 per cent. glucose and 13.9 per cent. sucrose.

October 14th, the Honduras gave 1.4 per cent. glucose and 14.5 per cent. sucrose.

It will be observed that the total sugars present had increased in the case of the Early Amber, from 8.2 per cent. to 16.1 per cent., between July 18th and August 13th; during the same period, the total sugar in the White Liberian had increased from 9.8 per cent. to 15.8 per cent. So, likewise, the total sugars in the Chinese increased from 7.4 per cent. upon August 6th, to 15.4 per cent. upon September 13th; and the Honduras, which, upon August 12th, gave 6.33 per cent. of sugars, gave upon October 14th, 15.9 per cent.

It appeared from these examinations, that when the maximum content of sugar had been attained, it was maintained by the plant during the remainder of the season, thus affording ample time to work up the crop for sugar.

Between the 13th of August and the 29th of October, there were made in all, fifteen examinations of the Early Amber, and during this period of 78 days, the average per cent. of crystallizable sugar in the juice was 14.6, the maximum being 17.0 per cent.

Between August 13th and October 29th, there were made in all, thirteen examinations of White Liberian, the average of all giving 13.8 per cent. of sucrose, with a maximum of 15.2 per cent.

Between September 13th and October 29th, there was made seven examinations of Chinese, the average of all, during a period of 46 days, being 13.8 per cent. of sucrose, the maximum being 15.05 per cent.

Between October 14th and October 29th, three analyses were made of the Honduras, which gave, during a period of 16 days, an average per cent. of sucrose of 14.6, with a maximum of 15.1 per cent.

For purposes of comparison, a bundle of sugar cane was obtained from the president of the Louisiana Sugar Planters' Association, consisting of three varieties of cane, viz: ribbon cane, plant of 1878 and 1879, and red cane, plant of 1879.

Triplicate analyses of each of these three varieties were made, and the average of the nine analyses showed an average percentage of sucrose of 14.43.

Analyses of thirteen specimens of sugar beets grown upon the Agricultural College farm at Amherst, Mass., and analysed by Professor Goessmann, gave an average per cent. of sucrose of 11.50.

It appears, therefore, from the above, that we have in these sorghums, a crop as readily grown as maize, and, when cut at the proper time, full as rich in sugar as the best Louisiana cane.

When the season was so far advanced that there was danger of frost, the remainder of the crop of these four varieties of sorghums was cut and worked for sugar, by processes similar to, if not identical with, those employed in the production of sugar from sugar cane; and in each case it was found that the syrups prepared by evaporation of the defecated juices of these plants, became, after standing from 24 to 36 hours, semi-solid, from the formation of crystals of sucrose; and in the case of the Chinese, the syrup yielded 55 per cent. of its weight in the first crop of crystals, a result altogether satisfactory, in view of the fact that this syrup had been prepared by open-pan evaporation.

As to the relative development of the sucrose and glucose in the butts and tops, it was found that in the early stages of the plant's development, the amount of sugar was greater in the butts, but that as the seed became ripe, the reverse became true, and the upper half of the stalks became richer in sugar, although the difference was at no time considerable.

Our experiments made with common field corn-stalks were most interesting, as indicating the possible utilization of what has hitherto been generally regarded, not only as a refuse, but to the large farmers of the West, a positive nuisance.

In the course of other experiments in the field, there was planted a small piece of corn, of the coarse growing White Dent variety. After the fully ripened grain had been gathered, the stalks, which were still green and juicy, were pressed, and the juice was found to contain 10.9 per cent. of sucrose and 2.4 per cent. of glucose. This juice, upon evaporation, gave a syrup which crystallized readily, and yielded at the rate of 960 pounds of sugar to the acre.

The shelled corn was at the rate of $69\frac{1}{10}$ bushels to the acre, 56 pounds to the bushel. Although the above yield of corn is not unprecedented, it is still far above the average yield per acre, and it is obvious that the value of the sugar obtained (which polarized 92°) is fully twice the value of the grain. From this it follows, that it is possible to secure, in sugar, fully twice the value of the grain which has hitherto been the only product which has been regarded as worth earning.

There are at present at the Department of Agriculture, thirty-six other varieties of sorghum seed received from different parts of the country, which have never been examined, and it is not improbable that among this number may be found those adapted to every variety of climate and soil where Indian corn may be grown. It is intended

to repeat the above examinations this year, and to examine these other varieties.

The practical results of the above investigations are, that for the production of either syrup or sugar from the sorghums, the cane should be worked when fully ripe, as evidenced by the seeds having become hard and dry, the lower blades of the stalks drying and falling away, and the appearance of off-shoots from the upper points of the stalks. At this period, not only is the total amount of sugars, both sucrose and glucose, at its maximum, thus giving the largest yield of syrup, but the relative proportions of crystallizable sugar to uncrystallizable, is also at its maximum, thus giving the largest yield of sugar.

X.—On Virulent Diseases, and Especially on the Disease Commonly Called Chicken Cholera.

By M. Pasteur.

Translated from the *Comptes Rendus de l'Academie des Sciences*, of Feb. 9th, 1880, page 239, by P. Casamajor.

Virulent diseases may be ranked among the greatest of the evils that afflict living beings. To prove this, we have merely to name measles, scarlatina, variola, syphilis, glanders, the carbuncular disease, yellow fever, typhus and the cattle plague. This list is far from being complete ; the pathology of the most important diseases may find a place here.

When the ideas of Liebig on the nature of ferments, were in vogue, each virus was considered as a substance undergoing an internal change, which could be communicated to living organisms, turning the constituents of these into a virus of the same nature. Liebig was well aware that the first apparition of ferments, their multiplication and their power of decomposition, present the greatest analogies with the phenomena of life, but, in the introduction to his Organic Chemistry, he tells us that these analogies may be considered as deceitful illusions.

All the experiments which I have communicated to this Academy for the last twenty-three years, have demonstrated, either directly or indirectly, the inaccuracy of the opinions of Liebig. A single method has guided me in the study of microscopic organisms. This method has been essentially the cultivation of these minute beings in a pure state, that is: by eliminating the heterogenous substances, living or dead, which accompany them. By the use of this method, the most difficult questions are often solved in the easiest and most

decisive manner. I will here recall one of the first applications which I made of this method (1857–1858).

Ferments, according to Liebig, are the nitrogenous substances of organisms, such as fibrine, albumen, casein, &c., in a state of decomposition, resulting from contact with air. There was no fermentation known, in which these nitrogenous substances were not present and active. One character of fermentations, as well as of diseases, was that they were spontaneous in their origin and development. In order to show that the hypothesis of the learned German chemist was, to use his own words, "but a deceitful illusion," I made up artificial mixtures whose only constituents were as follows: water, the mineral constituents essential to life, fermentable substances, and the germs of the ferments which act on these substances. With these mixtures, fermentation took place with a regularity and a purity, if I may use the word, which are never found in the spontaneous fermentation of nature. As every albuminoid substance had been excluded from these mixtures, the ferment appeared as a living being, which borrowed from the fermentable substance all the carbon of its successive generations, and, from the mineral constituents, the nitrogen, phosphorus, potassium, magnesium—elements, the assimilation of which is an indispensable condition to the formation of all living beings, be they great or small.

After these experiments, not only was the theory of Liebig left without any foundation, but the phenomena of fermentation presented themselves as simple phenomena of nutrition, taking place in exceptional conditions, the most extraordinary of which is the possible absence of any contact with air.

Human, as well as veterinary, medicine made use of the light which shone from these new results. Many investigators made experiments to discover if every virus or contagion was not an animated being. Dr. Davaine, in 1863, endeavored to show the functions of the *bacteridia* of carbuncular disease, which he had discovered in 1850. In 1868, Dr. Chauveau tried to show that virulence was due to the solid particles previously noticed in every virus. Dr. Klebs, in 1872, attributed traumatic virus to microscopic organisms. In 1876, Dr. Kock obtained, by artificial cultivation, the germs of *bacteridia*, which were similar in every respect to those which I had pointed out in *vibrios* (1865–1870), and the causes of several other diseases were ascribed to microscopic organisms. To-day those who are most opposed to the theory of germs, are wavering. Still the greatest obscurity prevails on the most important points.

In the great majority of virulent diseases, the virus has not as yet been isolated, and still less has it been shown, by artificial cultivation, that it is a living organism, and everything contributes to make us regard these "unknown quantities" of pathology as mysterious morbific causes. The study of the diseases which they cause, presents many extraordinary circumstances, among which the most remarkable is their non-recurrence. Human imagination can hardly venture to present a hypothetical explanation having any experimental foundation. Is it not still more surprising to find that vaccine, a virulent but mild disease, is a preventive, not only of vaccine itself, but of a more serious disease—the small pox? These facts were known from the remotest antiquity. Variolisation and vaccination have been practiced in India from immemorial times, and when Jenner demonstrated the efficacy of vaccination, the common people of the locality in which he practiced medicine, knew that cow-pox was a preservative from variola.

Vaccination appears as an isolated fact, but the non-recurrence of virulent diseases appears to be general. The organism does not go twice through measles, scarletina, typhus, the plague, variola, syphilis, &c.; at least it may be said that the immunity persists for a certain time.

Although in the presence of such mysteries, it behooves us to be humble, I dare to hope that the Academy will find that the facts which I am about to have the honor of presenting before it, throw unexpected light on the problems raised by the study of virulent diseases.

There occurs sometimes in poultry yards a fearful disease, commonly called chicken cholera. The victim overtaken by it, loses its strength, and stumbles about with drooping wings. Its feathers stand on end, and give it the appearance of a ball; it seems overcome by drowsiness; if we open its eyes, it seems to awake from profound sleep, and soon its eyelids close again. Generally death comes after a dumb agony, without the victim even moving from the position it has occupied during the last stages of the disease. In rare cases, it beats its wings for a few seconds. The internal disorders are of the most serious nature. This disease is caused by a microscopic organism which, according to Tundel's dictionary, was first suspected by M. Moritz, a veterinary surgeon in upper Alsatia; which was drawn more accurately, in 1878, by M. Peroncito, a veterinary surgeon in Turin; and which was found again, in 1879, by M. Toussaint, professor at the Veterinary School of Alfort, who demonstrated, by cultivation in neutralized urine, that this organism was the cause of the virulence in the blood.

In the study of microscopic parasites, the first, and most useful, condition to fulfil, is to obtain a liquid in which the infectious organism may be cultivated with ease, and without any admixture of other organisms of different species. Neutralized urine, which I have used with so much success to show that the product obtained by the cultivation of the *bacteridia* of Davaine, is identical with the virus of carbuncular disease (1877, Pasteur and Jaubert), does not fulfil the double end in view. But a liquid marvellously adapted to the life of the germ of chicken cholera, is a broth made from chicken's muscles, neutralized with potassa, and made sterile by a temperature superior to 100° C. (110° to 115°). The ease with which the microscopic organism multiplies in this liquid, seems prodigious. In a few hours, the most limpid broth becomes turbid, and is filled with an infinite multitude of small articulations of extreme tenuity, slightly thinner in the middle, and which at first sight have the appearance of isolated dots. These small articulations have no motion of their own, and they certainly belong to a very different group from that of *vibrios*. I imagine that they will be classified some day with other forms of virus, now unknown, when we cultivate these, as I hope we are on the eve of doing.

The cultivation of this microscopic organism presents some very interesting peculiarities.

In my former researches, one of the liquids which I used with the greatest success, was a decoction of beer-yeast in water, after filtering it to obtain it perfectly limpid, and after rendering it sterile by a temperature superior to 100° C. The most various microscopic organisms thrive on the food presented by this liquid, particularly after being neutralized. For instance, the *bacteridia* of carbuncular disease multiplies surprisingly in a few hours. It is a strange thing that this liquid is entirely unsuited to the life of the organism of chicken cholera, which dies in it in less than forty-eight hours. Is not this entirely analogous to what happens when a microscopic organism is entirely inocuous towards an animal on which it has been inoculated? It remains inoffensive because it does not develop in the body of the animal, and it does not reach the organs essential to life.

The sterility of the decoction of yeast, with respect to the microscopic organism of chicken cholera, affords us an excellent criterion for the purity of the cultivation of this organism in chicken broth. If the cultivation be pure, upon transferring it to a decoction of yeast, no development takes place, and the yeast solution remains limpid. If, however, other organisms are present, they are developed, and the

solution becomes turbid. I will, in the next place, call your attention to a still more extraordinary peculiarity of the cultivation of the germ of chicken cholera. The inoculation of this organism on Guinea pigs is not so surely fatal as in the case of chickens. In Guinea pigs, particularly in the older animals, the only thing that can be observed is a local lesion, at the point of inoculation, which ends in an abcess, of greater or lesser volume. This abcess opens spontaneously and heals, and meanwhile the Guinea pig eats his food as usual, and seems to possess all the characteristics of health. These abcesses last sometimes for several weeks before discharging, being surrounded by a membrane full of creamy pus, in which the microscopic organism exists in infinite numbers, side by side with the globules of pus. It is the life of the inoculated organisms which causes the abcess, which is as a closed vessel, from which we may obtain the organism without endangering the life of the animal. The microscopic organism remains, mixed with pus, in a great state of purity, without losing its vitality. This may be proved by inoculating on chickens a small portion of the contents of the abcess. From the effect of these inoculations, the chickens very soon die, while the Guinea pig, which has furnished the virus, is entirely cured after a short time. This is an instance of the localized evolution of a microscopic organism, which causes the formation of pus and of a closed abcess, without, at the same time, causing internal disturbances or the death of the animal on which it exists. It is, however, always able to cause the death of other species on which it may be inoculated, and even the death of the animal on which it exists in a closed abcess, if through some fortuitous circumstances, it should pass into the blood or into the viscera. Chickens and rabbits, living in company with Guinea pigs, affected with abcesses of this kind, might, all at once, sicken and die, without any great change being observable in the health of the Guinea pigs. This could easily happen if the abcesses of the Guinea pigs discharged a small portion of their contents on the food of the chickens and rabbits.

An observer who witnessed these facts, and was ignorant of all the points, might well be astonished to see chickens and rabbits die in great numbers, without any apparent cause, and he would be apt to believe in some spontaneous disease. Certainly, he would not suppose that the Guinea pigs were the cause of all the trouble, when he saw them all in good health, and particularly if he knew that the Guinea pigs themselves often suffer from the same disease. Many of the mysteries in the history of contagions will some day be solved in easier ways than the one I have just mentioned. We may reject

theories which are in contradiction with known facts, but we must not reject them solely because some of their applications elude our grasp. The combinations of nature are both simpler and more varied than those of human imagination.

I may easily convince you of the truth of these statements, if I add that, if a few drops from a cultivation of our microscopic organism, be placed on bread or meat given to chickens, they are sufficient to propagate the evil to their intestines, in which the little organism propagates with such remarkable rapidity, that the excrements of chickens so poisoned cause the death of those on whom they are inoculated. These facts enable us to understand the manner in which this fearful disease develops in poultry yards. Evidently, the excrements of the diseased chickens have most to do with the contagion. Nothing would be easier than to prevent the spread of the disease by isolating the chickens for only a few days; by washing the poultry yard with plenty of water, and particularly with water containing a little sulphuric acid, which kills the germ of this disease. The excrements should be carried off to a distance. After a few days, the chickens that are still alive could be brought together again with perfect safety, because this disease is so rapidly fatal that in a short time all the diseased animals would be dead.

If the cultivation of the infectious organism in chicken broth is repeated many times over, by passing from one cultivation to the next by sowing an infinitely small quantity, such as may be gathered on the point of a needle, the virulence of the germ is not weakened by the process. This is analogous to the ease with which it multiplies in the bodies of the *Gallinaceæ*. This virulence is so great, that the inoculation of a minute fraction of a drop will cause death in two or three days, and most generally in less than twenty-four hours.

Having established these preliminaries, I now come to the most important portion of this communication.

By operating certain changes in the process of cultivation, the virulence of the infectious germ may be much lessened. This is the vital part of the subject. I beg the Academy's permission to withhold a description of the processes by means of which I determine this diminution of virulence. My object is to insure independence in my studies.

The diminution of virulence is seen in cultivations by a slower development of the infectious organism, but, in reality, the two varieties of virus are identical. In the first or very infectious state,

the inoculated germ may kill twenty times in twenty. In the milder state, it may twenty times in twenty give rise to illness, but not to death. These facts have an importance which is easily understood, as they allow us to form an opinion, in this particular disease, of the problem of its recidivation or non-recidivation. If we take forty chickens, and inoculate twenty of them with the very virulent virus, these twenty will die. If we inoculate the other twenty with attenuated virus, these will all be ill, but they will not die. We let the twenty chickens be entirely cured, and then if we inoculate them with the very infectious virus, they will not die. The conclusion from this is evident. The disease is its own preventive. It has the character of virulent diseases, which do not recidivate.

Let us not be astonished at the singularity of this result. All things are not here as new as they appear at first. In one important particular, however, there is a novelty which will be pointed out. Before the time of Jenner, who himself practiced this method, as I have already mentioned, there was a practice of inoculating variola to preserve from variola. In our day, sheep are inoculated with murrain to preserve them from murrain, and cattle are inoculated with peripneumonia to preserve from this fearful disease. Chicken cholera shows us an immunity of the same kind. It is an interesting fact, but it does not show any theoretical novelty. There is, however, an important novelty in the preceding observations, a novelty which gives food for reflection on the nature of virus. It consists in this, that we have here a disease whose virulent cause is a microscopic parasite, which may be cultivated outside of the animal economy. The virus of variola, the virus of vaccine, those of glanders, syphilis, the plague, &c., are unknown in their nature.

This new virus is a living organism, and the disease to which it gives rise has one thing in common with virulent diseases, properly so called, a quality heretofore unknown in virulent diseases, caused by microscopic parasites: it is, that it does not recidivate.

The existence of this disease is a connecting link between virulent diseases caused by a living virus, and other diseases, in the virus of which life has never been recognized.

I would not have it believed that the facts present the constancy and mathematical regularity which I have mentioned. To believe this would be to ignore the great variability in the constitution of animals, taken at hap hazard from among domestic animals, and also the variability in the manifestations of life in general. The very virulent virus of chicken cholera does not always kill twenty times

in twenty. Sometimes this virus only kills eighteen times in twenty, but generally twenty times in twenty. We may also remark that the virus, when reduced in virulence, does not save life twenty times in twenty. Sometimes this happens only eighteen times in twenty and even sixteen times in twenty. Neither is it an *absolute* preservative by one inoculation. We may more surely prevent recidivation by two than by one inoculation.

If we compare the results above stated with what is known of vaccine and its relations to variola, we may see that the less vigorous organism which does not cause death, is analogous to a vaccine, relatively to the one that kills, for it gives rise to a disease which may be called mild, as it does not cause death, and, at the same time, it preserves from the disease in its most deadly shape. What other condition must this organism fulfil to be a true vaccine like that of cow-pox? This condition is that it should be a definite variety, and that we should not be obliged to prepare it *de novo*, when we wish to use it. We find here the same difficulty which presented itself to Jenner. After he had demonstrated that inoculated cow-pox is a preservative against variola, he thought that it was necessary to start from the cow-pox of a cow. Jenner soon discovered, however, that he could get along without cows, and make vaccine pass from one arm to another. We may try to do the same by causing our germ to pass from one cultivation to another. Under these circumstances, will the germ become actively virulent or will it remain moderately so? Although this may appear very astonishing, I can say that the last supposition is the correct one. The virulence of the germ, in the small number of cultivations which I have attempted, has not increased, and everything seems to point to the existence of a true vaccine. I may even add that one or two trials favor the idea that the attenuated virus keeps its character of mildness after passing through the bodies of Guinea pigs. Will the same thing happen after repeated cultivations and repeated inoculations? Only by experiments can such a question be answered.

At any rate, we now know of a disease caused by a microscopic parasite, which may be obtained in such a condition, that it does not recidivate, as other diseases caused by similar parasites. Moreover, we have a variety of its virus, which behaves towards it as vaccine towards variola.

The Academy may allow me a digression worthy of attention. From what has been said, we can easily obtain chickens affected with the disease called *chicken cholera*, in which death is not a necessary

consequence of the disease. We may then witness as many cases of cure as we may wish. Now, I do not believe that experimental surgery has ever met with more curious phenomena than those which are present when the animal returns to health, after inoculations have been made in the large pectoral muscles. The germ of the disease multiplies in the substance of the muscle as it would in a vessel. At the same time, the muscle swells, hardens, and becomes bleached at the surface and below the surface. It becomes filled with globules of pus, but does not suppurate. Its histological elements are easily torn, because the parasitical germ is scattered through them in numerous pockets, and it feeds on a portion of their substance. I will, later on, exhibit colored figures, showing the disorders caused by the parasitical germ in case of cure. The parasite is gradually arrested in its development and disappears, while at the same time the portion of muscle which has been attacked, unites, hardens and lodges itself in a cavity whose surface resembles that of a healthy granulating wound. The portion which has suffered from the disease finally forms a sequestrum, and is so well isolated in the cavity that holds it, that it may be felt by the finger under the skin, and, by the least incision, it may be seized with forceps and extracted. The small wound left in the skin heals immediately, and the cavity is gradually filled by the renewed elements of the muscle. I will now place some of these demonstrations before the Academy.

I have now to close by an explanation relating to the non-recidivation of the disease which occupies our attention. Let us take a chicken thoroughly vaccinated by one or more previous inoculations of the enfeebled virus. What will happen if we inoculate the same chicken again? The local lesion will be insignificant, while the first inoculations, and in particular, the very first, had been the cause of such marked change in the muscle, that a large sequestrum can be easily felt by the touch. The cause of the difference in the effects of these inoculations, is to be found entirely in a greater relative facility of the development of the germ of the disease at the first inoculations, and, in the last inoculation, in the development being either entirely wanting or very feeble and promptly stopped. The consequence of this seems evident, and it is that the muscle, which has been seriously diseased, has become, even after it has been cured, unfit for the cultivation of the germ of the disease, as if this germ, by a preceding cultivation, had suppressed some principle which life does not bring back, and whose absence prevents the development of the microscopic organism. I have no doubt that this

explanation, to which we are led by palpable facts in this case, will be found to be generally applicable to all virulent diseases.

It must appear superfluous to point out the principal consequences of the facts which I have had the honor to present before this Academy. There are, however, two of these which may be mentioned. One is, that we may hope to obtain artificial cultivations of every virus, and the other is, the idea of obtaining vaccines of the virulent diseases which afflict humanity, and which are the greatest plague of agriculture, in the breeding of domestic animals.

It is a duty and a pleasure for me to add, that in these delicate and lengthened researches, I have been assisted with great zeal and intelligence by Messrs. Chamberland and Roux.

Abstracts from American and Foreign Journals.

Bulletin de la Société Chimique de Paris.

Abstractor, E. H. S. Bailey, Ph.B.

Various Thermochemical Data, Berthelot (**32**, 385).—From his recently published work, the author gives various data, the result of careful experiments, in regard to the heat of formation of cyanogen, of diamylene in the gaseous state, and the heat of fusion of glycerine, and its specific heat.

On the Elimination of Bromine from Bromocitraconic Acid, and on a New Organic Acid, E. Bourgoin (**32**, 388).—By partially saturating a solution of bromocitraconic acid with caustic potash, and slowly evaporating the solution, crystals of bromide of potassium separate out, and the mother liquor consists of a new acid corresponding to the formula $C_{10}H_4O_8$. It appears to be related to pyrotartaric acid ($C_{10}H_8O_8$), and also to citraconic acid ($C_{10}H_6O_8$).

Note upon the Solubility of Benzoic and Salicylic Acids, E. Bourgoin (**32**, 390).—A re-assertion of facts previously stated, and a description of the methods used (see Bull. Soc. Chim., **31**, 53, and this Journal, **1**, 272).

On the Chlorhydrate of Phosphoretted Hydrogen, J. Ogier (**32**, 483).—In the apparatus devised by M. Cailletet, at a temperature of 14°, hydrochloric acid combines with phosphoretted hydrogen, producing hydrochlorate of phosphoretted hydrogen. It appears in the shape of small, snowy flakes. At a little higher temperature it is a liquid.

On the Heat of Formation of Bromohydrate and Iodohydrate of Phosphoretted Hydrogen, J. OGIER (**32,** 484).—These determinations were made with special reference to a comparison with similar ammoniacal compounds. The results are:

HCl gas + NH_3 gas	= NH_4Cl	disengages	+ 42.5	cal.
HBr " + NH_3 "	= NH_4Br	"	+ 45.6	"
HI " + NH_3 "	= NH_4I	"	+ 44.2	"
PH_3 " + HBr "	= PH_4Br	"	+ 23.0	"
PH_3 " + HI "	= PH_4I	"	+ 24.1	"

Or, if we take the elements simply, the results are :

Cl + H_4 + N	= NH_4Cl	disengages	+ 91.2	cal.
Br liq. + H_4 + N	= NH_4Br	"	+ 81.7	"
I sol. + H_4 + N	= NH_4I	"	+ 65.1	"
Br liq. + H_4 + P sol.	= PH_4Br	"	+ 44.1	"
I sol. + H_4 + P sol.	= PH_4I	"	+ 29.5	"

It will be noticed that the heat of combination of the ammoniacal salts is considerably higher than that of phosphorus compounds.

On the Pyridine Bases, AUG. RICHARD (**32,** 486).—Several homologous bodies having the general formula $C_nH_{2n-5}N$, have been discovered in animal oil from various sources. Some of these, as pyridine, picoline and collidine, have been formed synthetically, but it has not been fully determined whether these bodies are identical or isomeric. From a study of these bodies, and especially of collidine, the inference is drawn that they are isomeric.

Partial Synthesis of Sugar of Milk, and Contributions to the Synthesis of Cane Sugar, E. DEMOLE (**32,** 489).—Starting with the simple hypothesis, that in cane sugar and milk sugar the molecules of glucose are different and not identical, the author has made the attempt to unite levulose to dextroglucose, and galactose to lactoglucose. He has failed with the former, but succeeded with the latter. Two molecules of dextroglucose united, with loss of water, cannot form cane sugar. In the case of sugar of milk it is converted by dilute acid into two isomeric bodies, galactose and lactoglucose. By acting on this mixture with acetic anhydride, a body is produced having all the properties of octacetyl milk sugar, and agreeing very closely with the octacetate described by Schuetzenberger. If an alcoholic solution of this synthetically formed ether of milk sugar be treated with baryta, milk sugar is formed, which readily crystallizes from the solution after the removal of the excess of baryta. There is then a complete identity between the two octacetylic ethers and the sugars derived from them. The action of acetic anhydride upon the

glucoses seems to be that two molecules of glucose, either different or similar, in the presence of this dehydrating body, are changed to their anhydrides. Afterwards the action of acetic anhydride upon these anhydrides, changes them to an ether of diglucose, in the same way that oxide of ethylene absorbs acetic anhydride, producing an ether of diglycol.

On Chlorophyl, A. GAUTIER (**32**, 499).—This substance, as was shown several years ago, may be obtained in very perfect crystals. It presents many analogies to bilirubin, both in its reactions and in its elementary composition; the latter seeming to classify it as a higher isologue of that substance. The substance described by Hoppe-Seyler under the name of chlorophyllane, is probably simply chlorophyl. Pure chlorophyl does not contain iron. It seems to be related to hæmatin, the coloring matter of the blood.

On the Constitution of Dibromethylene, E. DEMOLE (**32**, 547).—The determination of the constitution of dibromethylene is of importance, as it will help to explain the phenomenon of oxidation which bodies undergo in contact with free oxygen at ordinary temperatures. In studying the action of benzine upon dibromethylene, in the presence of Al_2Cl_6, it is found that two atoms of bromine may be replaced by phenyl, giving

$$\begin{matrix} CH-C_6H_5 \\ \| \\ CH-C_6H_5 \end{matrix} \quad \text{or} \quad \begin{matrix} CH_2 \\ \| \\ C \\ \diagdown\ C_6H_5 \\ \quad\ C_6H_5 \end{matrix}$$

This hydrocarbon, $C_{14}H_{12}$, is either stilbene or diphenylethylene. On treating it with an acetic acid solution of chromic acid, and by saturating the excess of acid with carbonate of soda, drying and distilling, crystals of pure benzophenone are obtained. The above hydrocarbon is therefore disymmetric stilbene, and has the formula

$$\begin{matrix} CH_2 \\ \| \\ C \\ \diagdown\ C_6H_5 \\ \quad\ C_6H_5 \end{matrix}$$

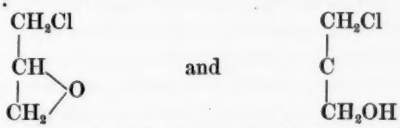
derived, of course, from dibromethylene, also disymmetric

$$\begin{matrix} CH_2 \\ \| \\ CBr_2 \end{matrix}$$

Since it is demonstrated that in dibromethylene the two bromine atoms are attached to the same carbon, it seems best to discard M. Fittig's explanation, which assumes that dibromethylene has two free affinities, and can take up oxygen, as follows:

$$\begin{matrix} CH_2Br \\ | \\ C-Br \\ \diagup\ \diagdown \end{matrix} + O = \begin{matrix} CH_2Br \\ | \\ C-Br \\ \diagup\ \diagdown \\ \quad O \end{matrix}$$

On the Constitution of Epichlorhydrine. HANRIOT (**32**, 550).—Two methods have been proposed to represent the constitution of this body, viz:



If, as the last method supposes, an alcoholic group exists, the body should be attacked by PCl_3, giving dichloride of isoallylene. If, however, it contains oxide of monochlorpropylene, it should not be affected by PCl_3.

Essentially, two bodies are obtained by this reaction. The first, boiling at 130–140°; the second, at 220°. The first has the formula C_3H_5OCl,PCl_3; the second, since it has no constant composition, is evidently dissociated. The combination of epichlorhydrine and PCl_3 is decomposed by water into phosphorous acid and epichlorhydrine. In the reaction of PCl_3 upon epichlorhydrine, no chloride of isoallylene was produced, hence confirming the formula as given by M. Reboul, viz., the first above mentioned.

Action of Sodium upon Epichlorhydrine, HANRIOT (**32**, 552).—The body $C_6H_{10}O_2$ can be separated from NaCl, which is obtained by the action of sodium upon epichlorhydrine, by crystallizing out the NaCl, and distilling the oily liquid with ether.

On Dimethylnaphtylamine and Naphtoquinone, P. MONNET, F. REVERDIN and E. NOELTING (**32**, 552).—Dimethylnaphtylamine was subjected to oxidation for the purpose of obtaining a coloring matter. Different methods of oxidation were used, with no success. A naphtoquinone was prepared by the oxidation of naphtylamine with $K_2Cr_2O_7$ and H_2SO_4.

On the Fermentations that take place in the Process of Extraction of the Saccharine Liquid from Beet Roots by Diffusion, A. MILLOT and MAQUENNE (**32**, 611).—It has been frequently noticed that in this process about 1 per cent. of the sugar is destroyed. In the case of the apparatus being partly empty, it has been noticed that sometimes an explosive mixture is formed. From the products obtained by distillation, the theory is advanced, that at the temperature at which this diffusion takes place, as long as oxygen is present, acetic fermentation goes on. As soon as the oxygen is exhausted, the fermentation ceases, and butyric fermentation proceeds, accompanied by the disengagement of carbonic anhydride and hydrogen. A little alcohol is also formed. The hydrogen is therefore produced

by butyric fermentation, and a small quantity may be also formed by the action of the acetic acid on the iron of the apparatus.

Transformation of Styrolene Bromide into Methyl Benzoate, C. FRIEDEL and M. BALSOHN (**32**, 613).—Some diversity of opinion has existed as to the constitution of monobromostyrolene made from styrolene bromide by the action of alcoholic potassa. From styrolene bromide, by the action of sulphuric acid, a small quantity of methyl benzoate was obtained. The decomposition succeeded better, however, if styrolene bromide was heated in sealed tubes at 180°, with a large excess of water. The oily part of the liquid, on being distilled at 200°, gave off a little more than one-half of the theoretical quantity of methyl benzoate. The reaction is expressed: $C_6H_5.CBr.CH_2 + H_2O = C_6H_5 - CO.CH_3 + HBr$. Styrolene bromide consists largely, therefore, of $C_6H_5.CBr.CH_2$.

On the Oxidation of Ethyl Benzine, C. FRIEDEL and BALSOHN (**32**, 615).—The author infers, that in oxidizing ethyl benzine it ought to be possible to obtain not an aldelyde, but an acetone, methyl benzole. This would take place if we suppose that of the two groups, CH_2 and CH_3, which are attached, directly or indirectly, to the benzine nucleus, the first is most readily oxidized. Upon oxidizing ethyl benzine by an acetic acid solution of chromic acid, and subsequent distillation, methyl benzole was formed. From a consideration of the facts of the case, it is concluded that in the oxidation of aromatic hydrocarbons, at least in those in which there is a CH_2 group attached to the benzine nucleus, an acetone is formed, which breaks up, as is readily seen. If, however, in the place of a CH_2 group, there should be a CH group attached to the benzine, and saturated by two other atoms of carbon, the oxidation would not give acetone, but without doubt a tertiary alcohol, by the simple addition of oxygen, without the elimination of hydrogen.

On the Synthesis of Ethyl Benzine by means of Ether and Benzine, BALSOHN (**37**, 617).—By heating together for some time at 180°, 1 part of ether, 2 parts of chloride of zinc, and 4 parts of benzine, there is obtained ethyl benzine, together with some undecomposed ether, benzine, and probably a little bi- or tri-ethyl benzine.

On the Direct Combination of Cyanogen with Hydrogen and the Metals, BERTHELOT (**33**, 2).—By heating a mixture of cyanogen gas and hydrogen, in a sealed tube at 500–550° for several hours, the two gases can be made to combine, producing hydrocyanic acid, $Cy + H = CyH$. Only a small quantity is changed to paracyano-

gen. Cyanogen also combines directly with the metals Zn, Cd and Fe, at 300°, if heated for some time in sealed tubes. With Cu, Pb, Hg and Ag, the combination is difficult to produce, probably because so high a temperature would be required as would cause a dissociation of the cyanogen gas. Cyanogen seems properly to have a double character, and to belong to both the formine and the ethylic series.

On Epichlorhydrine, BERTHELOT (33, 6).—A review and explanation of articles published elsewhere.

Berichte der Deutschen Chemischen Gesellschaft.

Abstractor, H. ENDEMANN.

On a Series of Aromatic Bases Isomeric with Mustard Oil and other Sulphocyanides, A. W. HOFMANN (13, 8).—In the preparation of Sell and Zierold's isocyanphenyl chloride by a modified method, using, instead of chlorine, phosphorus pentachloride, the author has obtained the above-mentioned compound, together with another substance, which on analysis proved to be monochlorphenyl sulphocyanide. Chlorine, as also sulphur chloride, did not produce this substance, and with phosphorus pentachloride but 18 per cent. of the theoretical quantity could be obtained.

Monochlorphenyl sulphocyanide is solid at ordinary temperatures, but melts at 24°. Vapor density, found, 82.4; calculated, 84.75. It forms crystallized salts with hydrochloric, sulphuric and nitric acids, and double salts with gold and platinum chlorides, which, however, are at once decomposed by the addition of water. A mononitro compound is produced by the action of nitric acid on a solution of the substance in concentrated sulphuric acid.

The chlorine atom is easily replaced by hydroxyl, by simple boiling with alcohol, or by ethyl, by the action of sodium ethylate.

By other well-known reactions, an amido compound, and an anilide, may likewise be produced.

The monochlorphenyl sulphocyanide loses, by the substitution of chlorine for hydrogen, its properties as a mustard oil. It does not, for instance, form compounds analogous to urea, nor does it lose its sulphur by the action of oxidizing agents, or give any other reaction which would prove its character as a simple derivative of mustard oil. Moreover, it has entirely different properties from all other products of the same atomic composition, derived from either para-, meta- or ortho-chloraniline.

The chlor-mustard-oil, under the influence of hydrogen in *statu nascendi*, gives again a substance of the composition of mustard oil, of basic properties, and otherwise differing from the mustard oil from which it has been derived. Experiments, made to determine the constitution of this substance, have so far failed to shed any light on this subject.

Synthetic Preparation of Formic Acid, V. MERZ and J. TIBIRICA (**13**, 23).—The authors have studied carefully the conditions under which carbonic oxide and alkalies produce the greatest yield of formates. They came to the following conclusions:

Carbonic oxide is absorbed by caustic alkalies at about 200°, formates being the result of the reaction.

In order to produce the most perfect possible saturation of all the soda, it should be used in the shape of soda-lime, as porous as possible. The carbonic oxide should not be dried, but should be kept moist by passing it through water. The temperature should not exceed 220°.

Above this temperature, carbonate and free hydrogen are formed. If, in the place of soda, potash is used, this reaction takes place already below 220°.

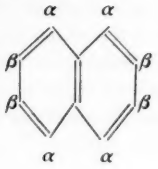
Experiments to produce benzoic acid from sodium phenylate and carbonic oxide, have failed.

A New Base, EDGAR F. SMITH (**13**, 33).—See this JOURNAL, **1**, 285.

Products obtained by the Nitration of Metachlorsalicylic Acid, EDGAR F. SMITH and G. K. PIERCE (**13**, 34).—See this JOURNAL, **1**, 288.

Normal Propylalcohol from Glycerine, ALB. FITZ (**13**, 36).—As products of fermentation of glycerine, the author obtained propylalcohol, beside ethyl- and butylalcohol, as before published.

On the α and β Position in Naphthalene, F. REVERDIN and E. NOELTING (**13**, 36).—The authors give in this short note, some additional reasons why the now generally accepted graphic formula for naphthalene,



as regards the α and β position in its various derivatives, should be retained.

On the Action of Sulphuric Acid upon Isomeric Nitramido- and Diamido-Benzoles, JUL. POST and E. HARDTUNG (**13**, 38).

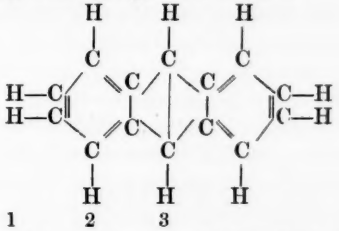
On the Detection of Alizarine, Isopurpurine and Flavopurpurine in Mixtures, and the Quantitative Determination of Alizarine, E. SCHUNCK and H. ROEMER (**13**, 41).—Will be noticed elsewhere.

Some new Azo-compounds, J. H. STEBBINS (**13**, 43).—See this JOURNAL, **1**, 465.

Lecture Experiment, H. SCHULTZE (**13**, 44).—The author describes an apparatus destined to show the condensation of gases, to an audience.

The Synthesis of Cumole, by AD. LIEBMANN (**13**, 45).—In order to prove the identity of isopropylbenzole with cumole, the author prepared it by the action of benzole chloride on zincmethyl. The identity of the isopropylbenzole thus obtained, was evident from the specific gravity, the boiling point, and the properties of the barium salt of the acid prepared therefrom, all of which coincide with the properties of cumole and its sulpho-derivative.

The Third Anthracene Monocarbonic Acid, by C. LIEBERMANN and A. BISCHOF (**13**, 47).—While but one benzole monocarbonic acid and two naphthalene carbonic acids are known, there should exist three anthracene monocarbonic acids, if the generally accepted graphic formula of anthracene be correct, according to the position of the carbohydroxyl group substituted for either one of the hydrogen atoms standing over the figures 1, 2 and 3.



Two of these acids have been already described. The authors have now obtained the third acid, possible according to the theory, by first reducing a commercial anthraquinonemonosulphonic acid, prepared by Meister, Lucius and Bruening, with the aid of hydrogen iodide, to anthracene monosulphonic acid, and converting this by distillation with dry prussiate of potash, into the nitrile, and the latter by the action of alcoholic potash solution into the anthracene monocarbonate. Further examination proved, that a mixture of two acids existed, one

of which gave an almost insoluble barium salt, and was found in this substance in quantity six times greater than that of the other, which gave a soluble barium compound. This acid has already been mentioned by Rath, but while he had obtained it rather as a by-product, it formed in this case the bulk of the material obtained. The analyses of the acid, and of the ethyl ether prepared therefrom, characterize it as anthracene monocarbonic acid.

Oxidation produces an anthraquinone carbonic acid, as in the case of the acid of Rath; it thus differs materially from the anthracene monocarbonic acid prepared by Graebe and Liebermann by the action of carbon oxychloride upon anthracene, which affords by oxidation, anthracene and free carbonic acid.

On the Composition of Manganese Peroxide produced by the Weldon Process, JUL. POST (**13**, 50).—The author gives a series of analyses of the product obtained by the Weldon process.

Contributions to the Knowledge of the Oxidation of Manganous Hydroxide with respect to the Method for the Regeneration of Manganese Dioxide, JUL. POST (**13**, 50).—The author considers it possible, that the absorption of oxygen is facilitated by the presence of a manganese oxychloride.

The Action of Sulphuric Acid on Phosphates, especially Calcium Phosphate, with respect to the Manufacture of Superphosphates, JUL. POST (**13**, 57).

Monophenylboron chloride and the Pentavalence of Boron, A. MICHAELIS and P. BECKER (**13**, 58). — Phenylboron chloride absorbs, at a temperature of 18° C., chlorine, which must be in chemical combination, as a current of carbonic acid gas does not remove it. On taking the glass, containing the compound, from the freezing mixture, chlorine is evolved, while phenylboron chloride and monochlorbenzole, remain. From the increase of the weight of the material, it appears probable that a phenylboron tetrachloride is formed, which is an additional fact in favor of the pentavalence of boron.

On Pyridine Carbonic Acids, S. HOOGEWERFF and W. A. VAN DORP (**13**, 61).—Tricarbopyridinic acid, obtained by the oxidation of quinine and the alkaloids associated with it, is decomposed into dicarbopyridinic acid and carbon dioxide, when heated to 185° or 190°, according to the formula $C_8H_5NO_6 = C_7H_5NO_4 + CO_2$. The properties of the acid and its salts make it probable that it is identical with the cinchomeronic acid of Weidel. Heating to 250° produces a further decomposition, the result of which is mainly a monocarbopyridinic acid, which the authors have called pyrocinchomer

onic acid, accompanied by another acid of the same composition, which may be nicotinic acid. The dicarbopyridinic acid produced by the oxidation of chinoline, furnishes, under the same treatment, only nicotinic acid.

Substances from Tar Produced by the Destructive Distillation of Animal Substances, H. WEIDEL and G. L. CIAMICIAN (**13**, 65).—The authors treat in this paper of those constituents of animal tar which are without basic properties. The fraction boiling between 98° and 150° furnished propionic, isobutyric, valerianic and isocapronic ethyl ethers, valeramide, also a peculiar substance furnishing with acids an india-rubber-like mass, then pyrrol, toluole, and ethyl benzole, and other hydrocarbons of the formulae C_9H_{14}, $C_{10}H_{16}$ and $C_{10}H_{14}$. All these substances constitute about 10 to 15 per cent. of the oil.

The next fraction, boiling between 150° and 220°, furnished mainly phenol, homopyrrol, dimethyl pyrrol, and also several of the higher hydrocarbons. This fraction is from 20 to 25 per cent. of the whole oil.

The third fraction, distilled between 220° and 360°, constituted from 60 to 70 per cent. of the oil, and, on examination, yielded beside some tar and ammonium cyanide and carbonate, especially the nitriles of palmitic, stearic and capric acids. There is hardly a doubt but that these are derived from the fats of the bones from which the tar was derived. The reaction by which these nitriles have been formed, may be expressed by the following formula:

$$C_nH_{2n}O_2 + NH_3 = C_nH_{2n-1}N + 2H_2O,$$

a reaction which can easily be demonstrated by distilling a fatty acid, and passing it, with a current of ammonia, through a red hot tube filled with pieces of pumice stone. No such compounds as pyrrol, or pyridine, are formed during this reaction. The presence of these substances must, therefore, depend upon the other constituents of the bones, notably the glue, and similar substances.

Action of Potassium Ferricyanide upon Morphine, K. POLSTORFF (**13**, 86).—Morphine is dissolved in water with the requisite quantity of caustic potash, applying heat gently; after cooling, a solution of a weighed quantity of ferricyanide of potassium is added, while a current of carbon dioxide passes through the liquid. A precipitate is formed, which, according to the authors, has been called oxydimorphine, and which results from the removal of two atoms of hydrogen. It is insoluble in water, alcohol, ether and chloroform. The reaction by which it is formed may best be described by the fol-

lowing equation: $2C_{17}H_{19}NO_3 + 2KOH + 2K_3^{'''}Fe(CN)_6 = 2H_2O + 2K_4^{''}Fe(CN)_6 + \begin{matrix} C_{17}H_{18}NO_3 \\ | \\ C_{17}H_{18}NO_3 \end{matrix}$ oxydimorphine.

Schuetzenberger's Oxymorphine, by K. BROOCKMANN and K. POLSTORFF (**13**, 88).—The authors have prepared oxymorphine by Schuetzenberger's method, and have come to the conclusion that the product of this reaction is not simply oxymorphine, $C_{17}H_{19}NO_4$, but oxydimorphine.

Action of Potassium Permanganate upon Morphine, K. BROOCKMANN and K. POLSTORFF (**13**, 91).—The result of this reaction is likewise not oxymorphine but oxydimorphine.

On the Action of Air upon Morphine in Ammoniacal Solution, K. BROOCKMANN and K. POLSTORFF (**13**, 92).—Oxydimorphine is formed.

On the Action of Potassium Ferrocyanide upon Methylmorphine Iodide, K. POLSTORFF (**13**, 93).—The result of this reaction is the basic iodide of methyloxydimorphine:

$$\begin{matrix} C_{17}H_{18}NO_3CH_3I \\ | \\ C_{17}H_{18}NO_3CH_3OH \end{matrix}$$

Methyl-morphine Hydroxide, K. BROOCKMANN and K. POLSTORFF (**13**, 96).

Action of Benzoyl Chloride upon Morphine, K. POLSTORFF (**13**, 98).—Morphine, heated for several hours with twice its weight of benzoyl chloride in a sealed glass tube, yields, after treatment with water and a slight excess of ammonia, tribenzoyl-morphine, $C_{17}H_{16}NO_3(COC_6H_5)_3$.

Acridine, C. GRAEBE and H. CARO (**13**, 99).—Acridine is oxidized only with difficulty. Although it has been held that a mixture of acetic and chromic acids, do not, even after long boiling, oxidize it, the authors found that, on continuing the operation for several days, oxygen may be added, the result of the operation being an indifferent body (*i. e.*, one devoid of either acid or basic characters), possessing apparently the formula $C_{12}H_{11}NO$, although the hydrogen was always found higher than theory requires. Distillation with zinc dust converts the product back into acridine. From its behavior it may be considered as a ketone. This reaction will be studied more thoroughly hereafter.

The oxidation of acridine may, however, be effected by the use of permanganate solution, care being taken to avoid an excess of this substance.

Thus a substance is formed, called by the authors acridinic acid, which crystallizes with 2 molecules of water: $C_{11}H_7NO_4$. It is bibasic. On heating to 130°, it loses one molecule of CO_2, leaving a monobasic acid, $C_{10}H_7NO_2$. On heating with slaked lime, 2 molecules of CO_2 are taken out, and chinoline is formed. Acridinic acid must, therefore, be considered as chinolinebicarbonic acid. The authors have also proposed a structural formula, but as they are now continuing their work, and desire to give their theoretical reasonings regarding this subject in another article, this fact is simply mentioned.

Artificial Alkaloids, A. LADENBURG (**13**, 104).—If tropine tropate be heated with diluted hydrochloric acid, an alkaloid is produced, which has the same composition with atropine, and has many properties in common with this long known alkaloid. As regards the physiological action of the new alkaloid, the study of which was undertaken by Professors Hensen and Falk, its identity was likewise established.

The author has also prepared a salicyltropeine, which has but weak poisonous properties, and an oxytoluyltropeine or homatropine, which is formed by the action of diluted hydrochloric acid on tropine formo-benzoylate. The physiological action of the latter alkaloid is very energetic, and the same as that of atropine.

The author has commenced the examination of hyoscyamine, and has, so far, ascertained that it is isomeric with atropine, but not identical therewith.

Hyoscyamine, when decomposed with baryta, forms hyoscynic acid, which has already been described, but, probably owing to impurities, its properties have not been correctly stated. It certainly does not melt at 104° to 105°, but above 116°. It has the composition of tropaic acid, and is probably identical therewith.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office**, by ARNO BEHR.

February 3, 1880.

224,014.—*Process of manufacturing fine salt.* THOMAS HIGGIN.

A mechanical process of disintegrating the coarse or lump salt, followed by sifting.

224,036.—*Process of manufacturing buttons and other articles from fibrous material and powdered hoof.* WILLIAM F. NILES.

224,101.—*Process for the manufacture of sulphate of soda.* WILLIAM T. MENZIES.

Brief: This manufacture is based upon improvements in the treatment of salt cake and nitre cake, so as to obtain a pure sodium sulphate free from acidity, and not containing an iron salt.

224,170.—*Manufacturing paper pulp from pine leaves.* CHARLES FULTON.

The claim gives no idea of the process.

224,186.—*Manufacture of beer.* GEORGE C. HOLDERER.

The first and second fermentations are effected at a temperature of from 41° to 68° F. After the beer has lost its new taste, the temperature is reduced to about 32° F., and the beer charged with carbonic acid.

224,240.—*Manufacture of carbonates and bicarbonates.* ALBERT STEARNS.

The absorption of carbonic acid by solid substances is facilitated by moulding these substances into blocks, which are perforated by a number of holes.

224,246.—*Production of cold in ice machines.* C. M. TESSIÉ DU MOTAY and AUGUSTE T. ROSSI.

The inventors have found that ether dissolves a large proportion of sulphurous acid gas at ordinary temperature and pressure. They use the resulting liquid in ice machines. In the working of the machine, the vapors of sulphurous acid and ether pass over into the condenser and cooler together, and are easily condensed under formation of the original liquid, a slight pressure only being required, owing to the chemical affinity between the two substances.

224,263.—*Electro-deposition of nickel.* JOSEPH YATES.

Claims the use of a solution of acetate of nickel.

February 10, 1880.

224,295, 224,296 and 224,297.—*Water-proofing and moth- and water-proofing compounds.* DANIEL M. LAMB.

A solution of paraffine in naphtha, or of caoutchuc in naphtha, or a mixture of the two solutions, is treated with hydrochloric acid gas. After the treatment, air is blown through the solution and the yet remaining acid removed by washing with water and alkali.

224,328.—*Galvanic battery cell.* GEORGE A. CONVERSE.

224,343.—*Galvanic battery.* WASHBURN MAYNARD.

Claim: A galvanic battery composed of a zinc positive, and a platinum plate surrounded by a mass of retort carbon in grains, these elements constituting a complete battery, for use with a suitable exciting liquid.

224,404.—*Galvanic battery.* JOHN DOYLE.

224,419.—*Process for manufacturing alcoholic spirits.* JOHN R. GLADNEY.

To the mash is added "California beer seed for generating a rapid vinous fermentation."

224,426.—*Manufacture of hydrogen sulphide.* W. E. A. HARTMANN.

Claims the production of sulphuretted hydrogen for industrial purposes, by bringing together at a red heat, in a suitable apparatus, sulphurous acid, "carbon in a liquid form," and steam.

February 17, 1880.

224,549.—*Process of making white pigments from lead sulphurets.* GEORGE T. LEWIS.

Passes powdered galena, intimately mixed with air, through retorts heated externally. The resulting fumes are collected in suitable apparatus.

224,611.—*Apparatus for effecting interchange of temperatures of fluids.* STANISLAS H. ROUART.

224,649.—*Composition for aiding the ignition of coal, etc.* JOHN M. CHILD.

A compound of ammonium sulphate, soda ash, saltpetre and ammonium nitrate.

224,660.—*Artificial stone.* T. PHELPS DAVIS.

Re-issue 9,075.—*Malt extract.* JOHN CARNRICK.

The extract is made from malted barley, wheat and oats, and contains all the soluble albumen of the grains in solution. This result is reached by conducting the conversion and evaporation at a temperature not exceeding 120° F.

February 24, 1880.

224,766.—*Vapor motor.* EDWIN M. BRADY.

Claim: A mixed vapor, adapted for use as a motor for machinery, the same consisting of vapor of bisulphide of carbon and vapor of saponified paraffine oil.

224,841.—*Compound for removing paint or varnish.* WILLIAM H. NORDABY.

Consists of lime, sal-soda, aqua-ammonia, creosote and water.

224,883.—*Compound for preserving fruit.* JOSEPHUS CRAFT.

Ten grains each of bisulphite of calcium and biborate of sodium, dissolved in one ounce of glycerine. This is added to one quart of sugar syrup, heated to 200° F., and poured over the fruit.

224,927.—*Dye-stuff or coloring matter.* FRIEDRICH KOEHLER.

A bluish-red coloring matter produced from the sulpho acid of diazo-azo-benzole and a bisulpho acid of beta-naphthole.

224,928.—*Dye-stuff or coloring matter.* FRIEDRICH KOEHLER.

A red coloring matter produced from the sulpho acid of diazo-azo-benzole and beta-naphthole.

Foreign Patents.

Condensed from R. BIEDERMANN'S Report to the German Chemical Society, by OTTO H. KRAUSE.

CARL LOEWIG, Breslau: *Clarification of beet and cane juice, syrup, &c.* (Germ. P., No. 8033, December 17, 1878.)—1,000 parts of cane juice are treated with 2 parts of lime, 1¼–1½ per cent. of colloid alumina, and, after a few minutes, slowly heated to 60° and 70° C. The deposit formed, contains the acids previously in combination as potassium salts, coloring, and other organic matters. Hydrofluosilicic acid or basic aluminium chloride is added to the filtrate, for the purpose of removing or neutralizing alkalies.

The juice can be evaporated immediately, or it may be still further improved by filtration through bone black.

The same treatment may also be applied to the intermediate products of the refining process.

Molasses or syrup is first diluted to 40° or 50° Brix, 1 per cent. of lime, and then colloid alumina added, until a filtered sample remains clear upon addition of basic plumbic acetate.

The filtrate passed through bone black, or treated by the osmose process, and evaporated, is said to yield an odorless syrup, from which sugar crystallizes out liberally.

EMIL JACOBSEN, Berlin: *Method of preparing sulpho acids of rosaniline, and coloring matters derived from them, and of alizarine and of purpurine, by the action of sulphuric chlorhydrate.* (Germ. P., No. 8764, March 1, 1879.)—Equivalent quantities of rosaniline, substituted rosanilines or their salts, alizarine or purpur

ine, are added to sulphuric chlorhydrate, contained in a cooled vessel, provided with a stirrer. The reaction is completed by warming the mixture upon the water-bath, and the sulpho acid obtained in known manner.

GRIPEKOVEN & Co., Brussels: *Artificial leather for lithographic rollers.* (Germ. P., No. 8738, July 31, 1879.)—20 parts syrup, 20 parts glue, 3 parts nitrate of potash, 3 parts sugar, 5 parts water, 1 part almond oil and 1 part chrome yellow, sulphate of alumina and potash, are heated upon the water-bath, and a hollow cylinder, the walls of which are about one-half inch thick, is formed of the mixture. It is then left for ten hours in a solution of sulphate of alumina and potash, and dried in the air.

PAUL GONDOLO, Paris: *Extraction of tannine.* (Germ. P., No. 7864, April 2, 1879.)—The water used is acidified with 0.6 per cent. sulphuric acid, the neutralized extract clarified by a small quantity of blood or gelatine, filtered and concentrated in air or in vacuo.

ALBERT CHRISTIANS and HEINRICH REINHOLD, Hamburg: *Coating for blackboards.* (Germ. P., April 27, 1879.)—A varnish, containing gum copal, shellac, venice, turpentine, lampblack and emery, is applied in two coats, the first being ignited and burned away before the second permanent one is laid on.

LAMBERT VON BABO, Freiburg: *Collodion covering for segars.* (Germ. P., Aug. 8, 1879.)

GILB. HUMPHREY COMFORT, London *Effervescent beverage.* (Engl. P., No. 73, January 7, 1879.)—Milk charged with carbonic acid.

WILLIAM RIDDLE, London: *Preservation of meat, milk, &c.* (Engl. P., No. 25, January 2, 1879.)—Meat is impregnated with carbonic acid, in a vessel from which the air has been exhausted. Milk is neutralized by addition of sodium bicarbonate, a little sugar added, and impregnated with carbonic acid. Hides are treated under pressure with solutions of aluminium chloride, or magnesium or zinc sulphate.

SYLVESTER FULDA, London: *Preservation of food.* (Engl. P., No. 347, Jan. 28, 1879.)—Claims mixtures of alum, silicate of soda, borax, cream of tartar, isinglass, lime and glauber's salts.

CHARLES CAMOYANO, London: *Furniture polish.* (Engl. P., No. 364, Jan. 29, 1879.)—Mixture of beeswax, turpentine, linseed oil, vinegar, chloride of antimony and wood spirit.

LEON FARGUE, Paris: *Ink compound.* (Engl. P., No. 526, Feb. 10, 1879.)—Aniline colors, soluble in water, are mixed with glycerine to a plastic mass, which is pressed into the pens.

OTTO STREUBEL, Paris: *Vegetaline.* (Engl. P., No. 127, Jan. 11, 1879.)—A substitute for ivory, caouchouc, leather, &c., and less combustible than celluloid. Cellulose is treated with sulphuric acid of 58° Bé at 15° C., washed, dried and ground, and the powder mixed consecutively with resin soap and sulphate of alumina, to form resinate of alumina. The mass is then pressed, and cut into slabs for use. To increase the incombustibility of it, silicates and borax may be added.

JAMES BALLANTYNE HANNAY, Glasgow: *Compound for preventing the destruction of ships' bottoms, or other submarine objects.* (Engl. P., No. 5088,

Dec. 12, 1878.)—60 parts alcohol, 9 parts shellac, 4 parts rosin, 3 parts gallipot, 2 parts soft gallipot. 4 parts arsenite of copper, 3 parts arsenite of mercury, 9 parts chromate of mercury, and 6 parts coloring matter.

HANS WEGENER, Weitendorf: *Apparatus for the production of high temperatures.* (Germ. P. of August 19, 1879.)—The object to be heated is exposed in a cylindrical vessel to the action of an oxyhydrogen blowpipe, under pressure. The pressure is produced by repeated explosions of small quantities of gun-cotton.

ERNEST GASTON BONG, Paris: *Method and apparatus for the reduction of alkaline and earthy sulphates.* (Engl. P., No. 845, March 6, 1879.)—The sulphates are heated in a system of chambers, and subjected to the action of sulphuretted hydrogen and generator gases (crude coal gas). The latter yield carbonic acid, which converts some of the sulphide in the moment of its formation, into carbonate.

The sulphurous acid formed during the reduction is free from air. The inventor claims that, by increasing the reducing agent, sulphur may be obtained. By mixing alkaline with earthy sulphates, fusion of the alkaline sulphides is avoided.

If silicates, clay and the like, be added to the sulphates treated by this process, silicates or aluminates of the alkalies or cement may be obtained.

ANTON ZENISEK and C. SCHMIDT, Dobrowitz: *Apparatus for manufacturing hydrofluosilicic acid.* (Germ. P., No. 9072, May 30, 1879.)—Silicium fluoride is generated in a long cast-iron retort, having the same cross-section throughout that part of its length which contains the charge. The ends of the retort are closed by cast-iron plates, and connected with a vessel containing water, and provided with a suitable stirring apparatus.

LARS W. BECK, Antwerp: *Method and apparatus for making assimilable phosphates.* (Engl. P., No. 814, Feb. 28, 1879.)—Sulphurous acid from a pyrites furnace is injected into water containing the raw phosphates. Calcium bisulphite and acid calcium phosphate are formed, and precipitated by the action of steam or hot air from the solution drawn off into another vessel. The sulphurous acid evolved is used over again. (The precipitation by heating of phosphates, dissolved in aqueous sulphurous acid, was first proposed by Gerland, see Wagner's Jahresber., 1864, 186, R. B.)

KARL ADOLF RIEBECK, Halle: *Method of purifying mineral oils.* (Germ. P., No. 9078, July 12, 1879.)—Creosote and similar matters are removed by treatment with solution of chloride of lime in alcohol, and with caustic soda.

C. HABER, Ramsbeck, Westphalia: *Method of separating iron and copper pyrites from mixtures with other minerals.* (Germ. P., August 21, 1879.)—Iron and copper pyrites are roasted, and the magnetic oxides removed from the mixtures with the aid of magnets.

LAMBERT HERLITSCHKA, Bautzen: *Furnace and method of fusing and refining metals.* (Germ. P., No. 18, Feb., 1879.)—The inventor claims the use of hydrocarbons as reducing agents for metallic oxides and sulphides, also sulphur and phosphorus, or sulphides and phosphides, in presence of superheated steam, as fluxes.

FERD. HECKEL and OSCAR OTTMANN, Neustadt: *Apparatus for the manufacture of illuminating gas.* (Germ. P., No. 8865, May 13, 1879.)—Hydrogen gas, evolved from iron filings and dilute sulphuric acid, in a tank lined with lead, is collected in a gas-holder, and passed through a vessel containing cotton saturated with gasoline.

JOS. BINON and ALPH. GRANDFILS, Stolberg: *Method of conglomerating mixtures of zinc ore and coal.* (Germ. P., No. 8703, July 5, 1879.)—The charge of zinc ore and coal is mixed with dry tar, and heated until the latter liquifies. The doughy mass is pressed in moulds to forms which exactly fit the interior of the zinc muffles.

OTTO S. HELLWIG, Brooklyn: *Improvements in furnaces for burning waste.* (Germ. P., No. 8810, July 17, 1879.)—A cast-iron plate or cast-iron pipe, fitted into the fireplace of a furnace, becomes heated to whiteness, and then heats and ignites gases that may have escaped complete combustion.

A. RUEMPLER, Hecklingen: *Removal of pectine substances from solutions of inorganic salts.* (Germ. P., No. 9075, June 15, 1879.)—Caustic soda solutions, from dye-works, &c., are freed from pectine substances, by precipitating the latter at the boiling point by means of magnesia, magnesium, carbonate or hydroxide. The magnesia is recovered from the precipitate by calcining it, or by solution in hydrochloric acid and fractional precipitation with milk of lime.

WILL. GARTON, Southampton: *Manufacture of starch, &c., from rice, corn and other amylaceous substances.* (Engl. P., No. 823, March 1, 1879.)—The substance is digested in cold water, placed in a closed vessel, with a 2 per cent. solution of ammonia, and heated to 50° C. for several days. The ammoniacal solution is drawn off and neutralized with acid, whereby fats and albumen are separated; by evaporation, ammoniacal salts are obtained. The rice, &c., is washed out, and used in the manufacture of starch.

HECTOR LEGRU, Paris: *Improvements in the preparation of saccharate of lime.* (Engl. P., No. 1266, March 29, 1879.)—In preparing saccharate of lime from syrup, the inventor uses little more lime than the quantity theoretically necessary, and adds inert matters, as native calcium carbonate, marl, brick-dust, bone black, and especially the dry calcium carbonate obtained in the decomposition of the saccharate of lime by carbonic acid.

CH. THOMAS, W. J. FULLER and S. A. KING, Bristol: *Extraction of glycerine from soap boilers' waters.* (Engl. P., No. 1282, March 31, 1879.)—The greater part of the salts contained in the waters is removed by evaporation and crystallisation, the remainder by boiling with a fatty acid in excess, whereby they separate as soap. The liquid is then filtered and distilled.

PETER KRAUS, Vienna: *Preservation of food* · (Engl. P., No. 1277, March 31, 1879.)—Consumes the oxygen in the air-tight vessels, by burning alcohol in them, and removes the products of combustion by an air-pump.

G. E. DAVIS, Heaton Moor: *Baking powder.* (Engl. P., No. 1249, March 28, 1879.)—Acid ammonium phosphate and alkaline bicarbonates, or calcium or magnesium carbonate.

G. W REYE & SONS, Hamburg: *Filtering tiles, from infusorial earth and gypsum.* (Germ. P., No. 9094, August 30, 1879.)—1 part gypsum and

3 parts infusorial earth are mixed to a paste, and allowed to harden. After the tiles have been used, they can be cleaned by washing or heating to redness. Impregnated with carbolic acid, they can be used for disinfecting purposes.

WILHELM BITTER, Bielefeld: *Improvements in apparatus for pharmaceutical laboratories.* (Germ. P., No. 8480, June 13, 1879.)—Arrangements for evaporating, distilling, boiling, &c. Apparatus for rapid drying by steam-heat.

CHARLES DE MONTBLANC and LUCIEN GAULARD, Paris: *Apparatus for the ammoniacal manufacture of soda.* (Germ. P., No. 8498, May 20, 1879.)—The apparatus admits of continuous working. Sodium chloride is placed in a tank, to the bottom of which water is admitted, through a perforated pipe. The solution of sodium chloride overflows into a second tank, which encloses the first, and contains a float, to regulate the flow of water into the first. From the second tank, the solution passes to the bottom of a vertical cylinder, to be impregnated with ammonia. Thence it flows into a series of connected cylinders, to be charged with carbonic acid. The end of the pipe which admits the gas is furnished with fans, to prevent the sodium bicarbonate from obstructing the holes.

JOHN CLIFF, Runcorn: *Improvements in sulphate furnaces.*—Replaces the double arch forming the roof by a single arch, composed of larger pieces of masonry.

WALTER WELDON, Rede Hall, Burstow: *Purification of alkaline lyes.* (Engl. P., No. 339, Jan. 28, 1879.)—To oxidize the sulphides in the crude lyes, a hydrated oxide of manganese (hydrate of Mn_3O_4) is added. The following reactions take place: $2Na_2S + Mn_3O_4 = 2Na_2O + 2MnS + MnO_2$, and $14Na_2S + 4Mn_3O_4 = Na_2S_2O_3 + 13Na_2O + 12MnS$. The manganic oxide is prepared by precipitating a solution of manganic sulphate or chloride, with lime or magnesia, and passing air through the mixture.

The manganic precipitate obtained in the purification of the lyes, is dissolved in hydrochloric acid, or it is added to the solution of manganic chloride, resulting from Weldon's method of preparing chlorine. (The above process is similar to the one patented by the Chemische Fabrik, Rheinau, see this JOURNAL, I, 588.)

THE AMERICAN CHEMICAL SOCIETY.

XI.—Proceedings.

The regular meeting, March 4th, 1880, was held in room 29, Cooper Institute.

The meeting was called to order at 8:30 P.M., Dr. Alsberg in the chair.

The minutes of the previous meeting were read and approved.

The following report of the last meeting of the Board of Directors was read:

Meeting of the Board of Directors of the American Chemical Society, *held February 26th, 1880, at the office of W. H. Nichols, 41 Cedar Street, New York.*

Present—W. H. Nichols, A. R. Leeds, P. Casamajor, E. Waller, A. H. Elliott, H. Endemann, C. F. Chandler.

Prof. A. R. Leeds in chair.

W. H. Nichols, Treasurer, asked to have a committee appointed to audit current bills. The Chair proposed that the committee of last year be retained. This proposition, being moved, seconded, and voted on, was carried unanimously. Messrs. E. R. Squibb and J. Goldmark were therefore retained as Auditing Committee for current bills, for 1880.

The meeting then discussed the means of raising funds for the maintenance of the Society.

At the suggestion of the Chairman, it was moved by W. H. Nichols, and seconded by E. Waller, "That a committee of five members be appointed to raise a permanent fund to defray the working expenses of the Society, and cost of publishing the Journal; and that the sum of $15,000 be raised by subscription, the collection of the amounts subscribed being made conditional upon the raising of the entire sum."

This motion was carried unanimously.

The following gentlemen were suggested as members of this committee: J. W. Draper, A. R. Leeds, E. R. Squibb, J. H. Stebbins, W. H. Nichols (ex-officio); as alternate, J. M. Maisch.

Mr. P. Casamajor, as one of the Committee on Rooms, reported the selection of a room in the Cooper Institute as perhaps suitable for the Society's meetings. Fears being expressed that the noise of the Elevated Railroad would be objectionable, P. Casamajor proposed, and W. H. Nichols seconded, the motion

"That the March meeting of the Society be held in the Cooper Institute, to see if the room be desirable."

This motion was carried unanimously, after which the meeting adjourned.

ARTHUR H. ELLIOTT,
Recording Secretary.

The Chair appointed Messrs. Rossi and H. Endemann, as tellers, to count vote on the election of J. V. V. Boraun, as associate member, and Everett B. Bragg, as active member; these gentlemen were reported duly elected.

Messrs. W. H. Nichols, H. N. Winans and Arthur H. Elliott nominated Mr. Alexander Cochrane and Mr. Hugh Cochrane, as associate members of the Society.

In the absence of Dr. Leeds, his paper on "Peroxide of Hydrogen and Ozone," as announced for this meeting, was not read.

The following papers were read:

1. "Action of Benzoyl Chloride on Primary Amines," by Jas. H. Stebbins, Jr.

2. "Action of Bromanile on Secondary and Tertiary Monamines," by Jas. H. Stebbins, Jr.

3. "On the Detection of Starch Sugar Mechanically Mixed with Refined Cane Sugar," by P. Casamajor.

After which the following papers were announced for the next meeting:

1. "On Peroxide of Hydrogen and Ozone" (second paper), by Prof. A. R. Leeds.

2. "On California Petroleum," by Dr. A. Bourgougnon.

The Corresponding Secretary then read an invitation from the Boston Academy of Arts and Sciences, to send three members of the American Chemical Society to represent it at the celebration of the 100th anniversary of the Academy. The Chair appointed Messrs. Sharples, C. A. Goessmann and W. B. Hills, as such representatives.

The resignation of Thos. Egleston was read and accepted.

The sense of the meeting was then taken as to the desirability of taking the room then occupied, as a permanent place of meeting; a majority of the members did not think it desirable.

After which a vote of thanks from the Society was tendered to Miss Julia Corson, for allowing the use of the room, and the meeting adjourned.

ARTHUR H. ELLIOTT,
Recording Secretary.

XII.—Action of Bromanile on Secondary and Tertiary Monamines.

By James H. Stebbins, Jr., S.B.

A few months ago, my attention was attracted by an article in the *Ber. d. d. chem. Gesell.*, **12**, 1610, entitled "On Some New Dyes."

Since then, several other publications on the same subject have made their appearance, and can be found in *Die Chem. Industrie*, and *Dingler's Polytechn. Journal.*

The articles all describe purple, blue and green dyes, produced by the action of chloranile, on secondary, tertiary and benzylated monamines. This color-bearing reaction, may, therefore, be divided into three steps, viz.: 1st. The action of chloranile on tertiary amines. 2d. Its action on secondary monamines. 3d. Its action on benzylated monamines. The first yielding fine blue dyes, the second, violet, and the third, green dyes.

If one molecule of chloranile is allowed to react on two mols. of dimethylaniline, $C_6H_5N(CH_3)_2$, at the ordinary temperature of the air, a fine blue color is instantly perceived throughout the mixture; but if gently heated over the steam bath, the mass thickens and the color deepens, till, finally, a drop of the substance, withdrawn from the mixture, becomes hard and brittle on cooling, and assumes a fine bronze lustre.

At this point the reaction is ended, and the mass, after cooling, is broken up, introduced into a flask, and the excess of dimethylaniline is driven off by steam. The remaining substance is then dissolved in strong alcohol and thrown into cold water, which precipitates the coloring matter in the form of dark blue flakes. The precipitate thus formed is gathered on a filter, washed and dried.

It is insoluble in water, but easily soluble in alcohol and ether, and glacial acetic acid.

If treated with sulphuric acid, a sulpho acid is formed, which is likewise a fine blue dye, and easily soluble in water.

Methylaniline and chloranile, under the same circumstances as above, yield a violet dye, which is likewise insoluble in water, and yields a soluble sulpho acid.

Being struck with the beauty of these compounds, and the ease with which they are produced, I was naturally led to consider whether bromanile ($C_6Br_4O_2$) would, under the same circumstances,

produce similar results; and, with this view, the following experiments were made:

My first object was to find a method which would yield considerable quantities of bromanile, in the least amount of time. The following method was finally adopted:

1 part of phenol is added, little by little, to 10 parts of bromine and $3\frac{1}{2}$ parts of iodine (under water), and heated to 100° C. for 1 to 2 hours. The raw material, thus formed, is collected on a filter, washed with water, and then heated with CS_2. This dissolves out all impurities, and leaves the pure bromanile behind, in the shape of golden yellow leaflets.

This body being now produced, I was anxious to see whether it would produce a blue dye with methyldiphenylamine, and I proceeded as follows:

If one molecule of bromanile and two molecules of methyldiphenylamine are allowed to react on one another, at the ordinary temperature, the result, as in the case of chloranile, is a blue coloration throughout the mass; if heated on the steam bath, the mixture thickens, and assumes a fine bronze lustre, and, finally, becomes hard and brittle on cooling.

The mass is then broken up, placed in a flask, and the excess of methyldiphenylamine driven off by steam. It is then dissolved in 95 per cent. alcohol, and thrown in cold water, which precipitates the coloring matter in the form of deep blue flakes, with a bronze lustre.

This is insoluble in water, but easily soluble in alcohol, to which it imparts a beautiful blue color.

It dissolves readily in strong H_2SO_4, to form a sulpho acid. This latter is quite soluble in water and alcohol, and is a strong blue dye.

A compound similar to this is produced, if equal molecules of methylaniline and bromanile are allowed to react on one another.

The mixture is heated on the steam bath till it thickens, and is then poured (while still hot) on a piece of cold marble or glass.

On cooling, it can easily be broken up, and is then treated with a current of steam, or heated with dilute HCl, to remove the excess of methylaniline. It is then washed, dissolved in alcohol, and precipitated by cold water, in the shape of violet-blue flakes, with the same bronze lustre as the previous compound.

It is likewise insoluble in water, and easily soluble in alcohol, with a fine violet-blue color.

It is easily dissolved by strong H_2SO_4, but is partially re-precipitated by cold water. If, however, it is dissolved in fuming H_2SO_4,

heated for some time on the steam bath, and then poured into cold water, a clear blue liquid is obtained.

This liquid is neutralized with $CaCO_3$, and the $CaSO_4$ filtered off. The lime salt is then decomposed with Na_2CO_3, and the soda salt obtained, is evaporated to dryness. It is very soluble in water, and dyes silk and wool a fine violet-blue color.

It may, therefore, be seen from this that bromanile behaves in nearly the same way as its related compound, chloranile, on secondary monamines, and the difference of color was probably due to the impurity of my methylaniline, as the latter is very hard to obtain free from dimethylaniline.

However, the result on tertiary amines is very satisfactory, as it proves that nearly the same tints of colors are produced in both cases.

The dyes herein described are only few in comparison with what might be obtained; for, it will naturally be understood, that by substituting the methyltoluidines, xylidines and naphthylamines, for methylaniline, and, on the other hand, substituting the dimethyltoluidines, xylidines and naphthylamines, for dimethylaniline, etc., or using the benzylated amines, a large number of violet, blue and green dyes are here possible.

The nature of these bodies I have not yet had time to determine, but hope to do so ere long.

NEW YORK, Feb. 25th, 1880.

XIII.—ON THE DETECTION OF STARCH SUGAR MECHANICALLY MIXED WITH REFINED CANE SUGAR.

BY P. CASAMAJOR.

About a year ago we were often entertained by the daily press with accounts of the adulterations practiced by sugar refiners, and, among these adulterations, the one most generally used, as we were then told, was the mixing of refined sugar with starch glucose. I must confess that I never believed in such a practice; for, although I had tried to procure specimens of such sugars, I was not able to find any, and one or two specimens which were given to me, as of sugar so adulterated, turned out to be pure, so far as the presence of starch sugar was concerned. The idea that these sugars were so adulterated, very likely originated in the imperfection of the processes used to detect the presence of starch sugar.

This week, however, I have had the good fortune to come in possession of a sample of refined sugar largely adulterated with starch glucose. This sample was sent to Messrs. Havemeyer & Elder from St. Louis, and a slip of paper in the box gave the information that the barrel from which this sugar was taken was marked "Powdered Sugar, Manhattan Sugar Refinery, New York;" a refinery, of the existence of which I have not been able to find any proof.

The incredulity which I previously maintained as to the existence of adulteration with starch sugar, was based on the following considerations:

It is well known that if you have a sugar solution, you can only obtain from it, by the ordinary processes of refining, a quantity of crystallized sugar representing very nearly the difference between the cane sugar present and the soluble impurities. If you have, for instance, a sugar solution whose coefficient of purity is 90 per cent., the soluble impurities will represent 10 per cent. of the total of the substances in solution, and you can obtain, at the utmost, only $90 - 10 = 80$ parts of sugar from 100 parts of substances dissolved. Processes have been published whereby a greater yield may be obtained, but such processes require the use of alcohol or of large quantities of salts of magnesia, and they have never been used on any extended scale. As starch sugar in solution does not act otherwise than any other impurity in solution, the addition of it in a dissolved state to a sugar solution, can not have any other effect than to diminish the yield of sugar and increase that of molasses.

The only manner in which starch glucose can be mixed with refined cane sugar, so as to give a profit, instead of a loss, to the person effecting this mixture, is to mix the two substances in a solid state. Now, the starch sugar must either be added in large quantities—and then it seemed to me that it could be easily detected by the eye or by the taste—or it must be added in very small quantities, and then the difference between the price of sugar and that of starch glucose would not leave a profit proportional to the trouble. My experience with sugar refiners does not lead me to believe that the refiner exists who would adulterate his products by adding to them only one to two per cent. of starch glucose. Such a thing would not pay.

The object of this communication is to give a few easy processes for the detection of starch glucose in commercial sugar.

By the use of the optical saccharometer, the presence of starch sugar may be easily detected, when in quantities as large as in the sample in question. It is a dextro-gyrate substance, and no other

dextro-gyrate substance can be used to adulterate sugar with efficiency in such large quantities.

The direct test, by the optical saccharometer, gives 97 per cent. After inversion, the reading of the saccharometer is 9.8 per cent. to the left, at 21° C. If we add these numbers, we find, by Clerget's table, that they correspond to 80 per cent. of cane sugar. As the sugar is dry, the balance, 20 per cent., nearly represents the quantity of starch sugar, as, from the appearance of the sugar, there must be very little inverted sugar present.

I need not now consider the subject of inversion, as a means of ascertaining the actual quantity of cane sugar present in a sample of commercial sugar, as I have already had occasion, in a paper read before this Society, at our regular meeting of February of last year, to discuss this subject at great length.* I may, however, say that if this sugar had been, what we call in the sugar business, a *straight sugar*, 97 per cent. of sugar, after inversion, would have given at 21° C. —32.5°, instead of —9.8°. I call your attention to this to show of what precious help the process of Clerget is in cases of this kind. It is a sad truth that very many persons, whose occupation is the analysis of sugars, are either entirely ignorant of the process of Clerget, or do not know enough about it to use it when they need it.

This sugar, tested by the alkaline copper solution, gives 17 per cent. of reducing substances, calculated as glucose, which shows that the starch sugar mixed with refined sugar contained $\frac{17}{20} = 85$ per cent. of these reducing substances.

The process which I had the honor of describing before this Society, at our June meeting,† gives unsatisfactory results with sugar adulterated with starch glucose. This is due to the imperfect solubility of starch glucose in methylic alcohol. After grinding the sugar under examination with the standard solution for three minutes, the process gave 85 per cent. of pure sugar—a discrepancy from the result by the saccharometer (80 per cent.), which never takes place with straight sugars.

Besides these processes, which can only be applied by persons provided with scientific appliances, the presence of starch glucose,

* See JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 1, 26; also Chemical News, 39, 212–234; Sugar Cane, 11, 296; Moniteur Scientifique, Juin, 1879, 647; Stammer's Zeitschrift, Juli, 1879, 683.

† See JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 1, 205; also Chemical News, 11, 74, 97, 107, 131; Sugar Cane, 11, 531, 588, 693; Stammer's Zeitschrift, October, 1879, 957.

when used in such large quantities, may be readily detected by very simple processes, which may be applied by anybody who wishes to use such means as are always at hand.

One process for the detection of starch glucose consists in adding to the suspected sugar somewhat less than its own weight of cold water, and stirring for a few seconds. If starch sugar is present, it will be seen floating in the solution as white specks, which resemble crushed wheat. This appearance is due to the comparative insolubility of starch glucose in cold water, which allows it to remain undissolved quite a long time, and also to the fact that as the cane sugar present is crystalline, and its refrangibility is not very different from that of a sugar solution, the portion of it which remains undissolved is not so distinctly seen as the specks of starch sugar. These specks are best seen by using a beaker glass, and putting only enough sugar and enough water that we may be able to see light through the flat bottom of the glass. If a flat bottomed glass is not at hand, the observation may be made on a pane of glass.

This process for the detection of mixtures of starch glucose with cane sugar is so simple and satisfactory, that I might well be excused from giving another, but the one I am about to give is useful for the detection of other foreign substances in the products of refineries. This latter process is based on the fact, that the taste of sugar has a tendency to dull our perceptions of the taste of other substances mixed with sugar. So as to neutralize this effect of sugar, we may, before tasting a suspected sample, put a pinch of pure sugar in the mouth. If after this sugar is dissolved, but while we still perceive its sweet taste, we put on the tongue a pinch of sugar containing starch glucose, we distinctly perceive the bitterish taste of the glucose. The presence of chloride of tin in molasses or sugars, even when used in very small quantities, can be easily detected by its unpleasant bitter taste, if, before tasting the suspected products, we fill the mouth with the pure sweet taste of refined cane sugar.

XIV.—On the Chemical Cause of the Poisonous Nature of Arsenic.

By C. Binz and H. Schulz.

From the Berichte d. d. chem. Gesellschaft, **12**, 2199.

It appears that Liebig has hitherto been the only author who has proposed a theory of the poisonous action of arsenic. It is to be found in the first edition of his work on the applications of chemistry to agriculture and physiology, and is essentially as follows: Arsenious acid and corrosive sublimate possess, in the highest degree, the capacity to form solid compounds with albumen. By internal administration, the albumen of living tissues loses the capacity to undergo the transformations necessary to their existence. The life of important parts is thus destroyed, and the death of the whole organism follows. Latterly, Liebig has not maintained this view; it is, however, still to be found in certain chemical works. It is untenable, for the reason that a solution of arsenious acid, or of its salts, does not form the solid compounds or albuminates which Liebig assumed, although this is undoubtedly the case with corrosive sublimate and certain other substances. Moreover, there has not been observed a single instance of a precipitating action produced by arsenious acid on the constituents of the animal body, stronger than that which would be produced by carbonic acid. This non-existence of an arsenious albuminate is proven by the fact that one can, for instance, poison an animal by dropping an arsenical solution on the extremely sensitive conjunctiva of the eye, without producing, on the place where the poison has been introduced, any other appearance than a slight reddening. In the interior of the body, however, the destructive effects are most distinctly visible. They centre in the stomach, even in those cases when not a trace of the poison has directly come in contact therewith. Anatomical investigations have shown us that precisely those tissues in the body, which are specially endowed with the capacity to receive and utilize the oxygen of the blood, such as, more particularly, the glandular protoplasm, form the principal seat of the destructive action.

The neutral salts of arsenic acid are just as poisonous as those of the arsenious acid. According to some accounts, they are even more so.

Arsenious acid changes readily to arsenic acid, and the transformation proceeds still more readily in the inverse sense. This latter

process is effected by albumen in general, the former by the living albumen of animals and plants.

These facts were proven first outside of the organism, with separate parts of the same. Arsenic acid was reduced, when treated at the temperature of the body, with egg albumen and fibrine of warm-blooded animals. Fresh brain substance had the same effect. The tissue of the pancreas, of the liver, and the undecomposed protoplasm of vegetable organs, not only reduced arsenic to arsenious acid, but also oxidized the latter to the former. If those tissues which oxidize arsenious to arsenic acid, be previously heated in boiling water, they lose this property. Blood, hæmoglobuline and fresh fat possess neither the former nor the latter property.

This double action may also be observed on the living animals. The two stages of oxidation of arsenic are reciprocally changed by the action of the glands of the intestinal canal, which also belong to those parts of the organism which experience soonest and most severely the effects of poisoning. Those portions of the organism which are not, or only secondarily, affected during life, are not capable of effecting the oxidation of arsenious acid. The careful consideration of all of the individual results of our experiments, leads to the conclusion that the reciprocal transformations of these two acids (which we were the first to prove in the case of *animal* bodies) produce within the living albumen molecule, in which they take place, a violent oscillation of the oxygen atom, whereby the tissues are corroded to the extent of their complete destruction.

An exact parallel exists between arsenic and nitrogen in this respect. Nitric oxide is extremely poisonous; it is transformed by reception of oxygen into the powerfully oxidizing hyponitric acid. The latter destroys the tissues, while it is, in part, transformed back into nitric oxide. Throughout the whole process, the nitrogen is without direct action; it is merely the inert carrier and distributor of the powerfully aggressive, active oxygen atoms. Arsenic fulfils the same functions where it appears as the carrier of active oxygen, *i. e.*, every moment arsenious acid is converted into arsenic acid, and this back again into arsenious acid.

The differences existing between arsenic and nitrogen are those of degree only. The oxides of nitrogen corrode those portions of the organism where they are first introduced; the oxides of arsenic develop their activity only within the organism, and, as is well known, are externally corrosive only by prolonged action. The active oxygen of the oxides of nitrogen is detached in an instant; that of ar-

senic acid requires some time, and that is the reason why the latter completes its destructive action only within the organism. That such oxygen atoms possess poisonous properties, is evident from the well-known deleterious effects of ozone, when it enters the system in any other state than that of extreme dilution. The case has, furthermore, recently been proven to be the same with the salts of chloric acid. They give up to certain constituents of the body their three atoms of oxygen, become changed to chlorides, and thus exert a corrosive and destructive influence on the cells and the blood.

Viewed from this standpoint, there becomes apparent a remarkable correspondence in poisonous, and in chemical, behavior among the other members of the nitrogen group. It is already known that they exert in the body a poisonous action similar, in its minutest details, to that of arsenic, differing therefrom only in degree.

This rapid change in the state of oxidation has been proven in the case of antimony, bismuth and vanadium. No known facts are opposed to the assumption of a similar transformation, such as we have shown to take place in the body, in the case of arsenious acid. Phosphorus passes, as such, dissolved in fat, into the circulation and into the tissues. Within, as well as outside of, the body, it acts as an ozonising agent. There results therefrom a violent disintegration of the living albumen molecules, which manifests itself, precisely as in the case of the administration of arsenic in suitable medium doses, in a considerable increase in the production of urea, in the diminution of glycogen, in the disorganization of important cellular groups, etc. All the effects produced in the body by phosphorus and arsenic, and, as far as has been investigated, the different stages of oxidation of the other members of the nitrogen group, and the benefits which have been obtained by their cautious administration, may be explained by the local excitation of oxygen.

The details of these experiments, and the conclusions drawn therefrom, have been published in the *Archiv fuer experimentelle Pathologie und Pharmacologie* (Leipsic, July, 1879), II, 200–230.

XV.—On the Relations Existing between the Physical Properties and Chemical Constitution of Organic Substances.

[First Paper.]

By J. W. Bruehl.

From the Ber. d. d. chem. Gesellschaft, **12**, 2135.

For about eighteen months past I have been engaged in investigations on the correlations between the chemical constitution and physical properties of organic substances. At the meeting of the Association for the Advancement of Science (Naturforscherversammlung), at Baden-Baden, of this year (1879), I gave a short account of the results hitherto attained. A detailed paper concerning this subject will shortly appear in *Liebig's Annalen*, and it may, perhaps, be not without interest to the Chemical Society, to communicate, in the following, a condensed account of the contents of the paper in question.

My work has, so far, been restricted to the comparison between the specific gravity and the index of refraction of liquid bodies, and the optical refractive and dispersive properties deduced from these constants.

Among the physical properties of organic compounds, the index of molecular refraction—also called, "the equivalent of refraction"—has already been thoroughly investigated, chiefly by H. Landolt and J. H. Gladstone, and many interesting analogies between these physical properties and the chemical properties of the substances in question, have already been noted.

At the suggestion of Prof. Landolt I decided, therefore, to subject this district, in the first place, to renewed investigation. I communicate in this place only a few of the results that I have obtained by the comparison of the molecular refractive capacities. The results of the comparison of the other constants can be found in the *Annalen*.

The property that matter possesses of refracting light, is one that depends on its chemical composition—the quality and combining proportions of the elements; but it is also closely dependent on the density, so that the denser bodies are, as a rule, the more strongly refractive; it is furthermore dependent on the temperature. Now, we are not able, in the case of liquid (and solid) bodies, to investigate the influence of temperature on the refractive properties separately from that of density, because warming and dilation are correlative

processes, and the expansion of a liquid enclosed in a glass prism cannot well be prevented. For the comparison of the refractive power of these substances with their chemical constitution, it is necessary to use a measure that has been freed from the influence of temperature, and based on equal densities. Through numerous investigations of Gladstone and Dale, Landolt, Wuellner, and others, it has been shown that the index of refraction, diminished by unity, and divided by the density, $\frac{n-1}{d}$, represents for every substance a value independent of the temperature. It is constant alike for liquid, solid, and even gaseous bodies, so that it may be termed, for all three states of matter, a common measure of the *relative refractive power* or *the specific refractive capacity.*

In the case of substances of low refractive capacity, there may be substituted for n, in the above formula, the index of refraction for light of any particular wave-length (color), *e. g.*, for the red ray of the hydrogen light Hα, which coincides with the Frauenhofer solar line C. In the case of more strongly refracting bodies, on the contrary, none of the observed indices can be used for the purpose of comparing them in regard to their refractive power, as they are all influenced by dispersion. An index of refraction free from dispersion, is one for a ray of infinitely great wave-length.

If μ_{λ_1} represents the observed index for light of the wave-length λ_1, and μ_{λ_2} for such of the wave-length λ_2, we can, as is well known, in the case of not too strongly refractive substances, make, according to Cauchy:

$$\mu_{\lambda_1} = A + \frac{B}{\lambda_1^2}$$

$$\mu_{\lambda_2} = A + \frac{B}{\lambda_2^2}$$

whence follows:

$$B = \frac{\mu_{\lambda_2} - \mu_{\lambda_1}}{\frac{1}{\lambda_1^2} = \frac{1}{\lambda_1^2}}$$

$$A = \mu_{\lambda_1} - \frac{B}{\lambda_1^2}$$

wherein B represents the coefficient of dispersion, and A, the index sought, for a ray of infinitely great wave-length.

This value of A may now be introduced into the formula $\frac{n-1}{d}$ as the pure coefficient of refraction, independent of dispersion, in the place of the crude index of refraction, n. For each individual substance, the constant: $\frac{A-1}{d}$ will then be influenced solely by the chemical character, and will be independent of variations in density and dispersion, and also of temperature. This expression can, therefore, be accepted as a true measure for the optical refractive force of the substance.

If these constants be multiplied by the molecular weight, P, of the compounds, then will $P\left(\frac{A-1}{d}\right)$ be the refractive capacity computed on chemically comparable quantities; hence the molecular refractive capacity, or, as I shall hereafter call it, the *molecular refraction.*

In my experiments, the determinations of density and indices of refraction were always made exactly at 20°. The density was determined with perfect accuracy to the fourth decimal place. I represent this value, compared with water, at 4°, and reduced to vacuo by

$$d\,\frac{20}{4}$$

The indices of refraction were determined for the sodium light, and for the three light bands of the hydrogen spectrum, by the method of minimal deviation (*kleinster ablenkung*).

The measurements were made with the aid of an excellent spectrometer, by Meyerstein, of Goettingen, which permitted the determination of the indices, with accuracy, to the fourth decimal place, varying by a few units in the fifth place. During the observation, a fine thermometer was kept in the previously-warmed prism, which permitted the temperature to be determined with accuracy to 0.1°.

As a rule, the coefficient of refraction, A, was determined from the indices for the red hydrogen line, $H\alpha$, and the violet, $H\gamma$.

The substances employed were partly prepared by myself, partly obtained from the establishment of C. A. F. Kahlbaum, in Berlin. For the propargyl derivatives mentioned in the following, I am indebted to the courtesy of Mr. Louis Henry, of Loeven.

The greatest care was taken with regard to the purity of the materials employed, which was always tested by analysis.

Through the investigations of other observers, and, especially, through the numerous and carefully elaborated observations of Landolt, it has been proven that isomeric substances behave

similarly in regard to the transmission of light; that only the combining proportions, but not the mode in which the atoms are grouped, is of influence on the molecular refraction. From this it follows that the atoms in all compounds possess the same specific refractive capacity, no matter what the arrangement may be. Landolt has used this fact to determine the refractive power of the atoms from the observed molecular refraction of the compound bodies.

Substances were compared that differed from each other in composition by 1 carbon, 2 hydrogen, or 1 oxygen atom, and the difference in the molecular refractive powers gave directly, therefore, the atomic refraction of the individual elements. In this manner, Landolt obtained the following values, computed on a ray of infinitely great wave-length:

	Atomic Refraction r_A.
C	4.86
H	1.29
O	2.90

With the help of these constants, the molecular refraction of substances containing carbon, hydrogen and oxygen, $C_xH_yO_z$, may now be calculated by the equation: $R_A = 4.86\ x + 1.29\ y + 2.90\ z$; and, in fact, it was shown that the molecular refraction calculated in this manner, agreed, as a rule, very closely with those deduced from actual observation.

The results of these beautiful investigations of Landolt were confirmed, later, by Gladstone, who, by extending the investigation to inorganic substances, showed that in the case of the latter, the rule also holds good, that the molecular refraction is equal to the sum of the atomic refractions.

Later investigations of Gladstone have, however, shown that this law has its exceptions, and it became apparent that the number of these exceptions was, in the case of organic bodies, very considerable.

A series of compounds, belonging to different classes, such as the benzole derivatives, the terpenes, many alkaloids, essential oils and other substances rich in carbon, possess, as Gladstone showed, an exceptional optical behavior. The observed molecular refraction is greater than that computed from the sum of the atoms present therein.

No satisfactory explanation of this peculiarity has hitherto been offered, still less has any attempt been made to show a connection

between the chemical character of these compounds and their apparently abnormal optical properties, which latter are distinct for each class of these substances.

I have succeeded in discovering such a connection. It results, namely, from my investigations, that, under certain conditions, the grouping of the atoms is of essential influence on the molecular refraction of the substance, and that the relations between this physical property and the chemical constitution may be accurately followed out and expressed in simple numbers.

From considerations which need not here be stated, I arrived at the view that, in the so-called unsaturated compounds, those atoms which are repeatedly and directly combined with each other, must exert a greater effect on the transmission of light than those atoms which are combined with each valence to another one.

When, therefore, for instance, hydrogen atoms are subtracted from a hydrocarbon, in such a manner that the exit of each pair of atoms causes a double binding of neighboring carbon atoms, the molecular refraction of the compound becomes greater than that computed from its percentage composition.

If R_A represent the equivalent of refraction, computed from the empirical compositions of such an unsaturated hydrocarbon, a, the influence of a double binding on its molecular refraction, and x, the number of hydrogen atoms removed—therefore, in this case, also the number of the double bindings—, then, according to this view, the molecular refraction of a body of the general formula, $(C_nH_{2n+2}) - xH_2$, should be: $P\left(\frac{A-1}{d}\right) = R_A + x.a.$

Furthermore, according to this hypothesis, the constitution will have no special effect on the optical behavior of unsaturated compounds, in which there exist no multiple attractions between neighboring carbon atoms, but wherein the exit of constituents from the saturated substance, results in a combination of carbon atoms not previously directly combined with each other. Their molecular refraction will correspond to the empirical composition: $P\left(\frac{A-1}{d}\right) = R_A$.

Substances of the formula, $(C_nH_{2n+2}) - xH_2$, in which not only multiple binding between neighboring carbon atoms, but also attraction between remoter carbon atoms, exists, will, therefore, if y be the number of pairs of hydrogen atoms, the elimination of which leads to the formation of a ring-like binding, and hence can have no special influence on the optical properties, possess the molecular refraction:

$$P\left(\frac{A-1}{d}\right) = R_A + (x-y).a.$$

For instance, in hexylene [in general in the olefines of the series $(C_nH_{2n+2}) - H_2$], there is a doubly bound carbon pair. The molecular refraction of this body should therefore be :

$$P\left(\frac{A-1}{d}\right) = R_A + a.$$

In diallyl, a body of the formula $(C_nH_{2n+2}) - 2H_2$, there are two carbon double bindings ; the molecular refraction should therefore be:

$$P\left(\frac{A-1}{d}\right) = R_A + 2a.$$

On the contrary, in benzole, and its derivatives of the formula $(C_nH_{2n+2}) - 4H_2$, a ring-shaped combination of the atoms is assumed, and only three double bindings ; in these bodies, therefore, $x - y = 4 - 1 = 3$, and according to the view previously mentioned, the molecular refraction of these bodies should be :

$$P\left(\frac{A-1}{d}\right) = R_A + 3a.$$

This hypothesis has, in general, been confirmed by experiment. It has become apparent that the refractive power of the atoms, of which the affinity is completely saturated, remains constant, no matter how they may, in other respects, be combined ; that, on the contrary, the atomic refraction is altered by incomplete saturation of the valence.

In this communication, only the influence of the multiple binding between carbon atoms will be considered ; the case of oxygen will form the subject for a future paper.

In the following table, under the heading, "substances with one carbon double binding," are given a number of such substances belonging to several different series:

SUBSTANCES WITH ONE CARBON DOUBLE BINDING.

I.	II.	III. $P\left(\frac{A-1}{d^{\frac{20}{4}}}\right)$	IV. R	V. Diff.
Ethylene perchloride.....	C_2Cl_4	49.7	47.8	+ 1.9
Allyl alcohol.....	C_3H_6O	27.1	25.2	1.9
Acrolein.....	C_3H_4O	25.3	22.6	2.7
Allyl-ethyl ether.....	$C_5H_{10}O$	42.2	40.1	2.1
Allyl acetate.....	$C_5H_8O_2$	42.2	40.4	1.8
Allyl chloride.....	C_3H_5Cl	32.6	30.6	2.0
Methacrylic acid.....	$C_4H_6O_2$	35.1	33.0	2.1
Amylene, 34–35°.....	C_5H_{10}	39.3	37.2	2.1
			Mean....	+ 2.1

Column III. contains the molecular refraction found; IV., that calculated by addition of the refractive capacities of the atoms.

In the foregoing calculations of R_A, the following values were employed as the atomic refraction of the elements:

	Atomic Refraction r_A.
C	4.86
H	1.29
O	2.90
Cl	9.53
Br	14.75
N	5.35

of which those for carbon, hydrogen and oxygen, were determined by Landolt; for chlorine and bromine, by Haagen; and for nitrogen, by myself.

Column V. of the table contains the difference between the observed and the calculated molecular refraction: $P(\frac{A-1}{d}) - R_A$. It will be noticed that these differences are always positive, and that they differ in general very little from the mean + 2.1.* From these numbers we have, therefore, the result that:

The molecular refraction of a substance containing one carbon double binding, is greater by about two than that calculated from the sum of the specific refractive capacities of the constituent atoms.

$$M_A = P(\frac{A-1}{d_4^{20}}) = R_A + 2.$$

The next table is divided into two compartments. In the upper are given the "substances with two carbon double-bindings." The lower contains a number of "substances with three carbon double bindings," collectively benzole derivatives. The arrangement of the table is the same as in the previous one:

SUBSTANCES WITH TWO CARBON DOUBLE BINDINGS.

I.	II.	III. $P(\frac{A-1}{d_4^{20}})$	IV. R_A	V. Diff.
Valerylene	C_5H_8	38.7	34.6	+ 4.1
Diallyl	C_6H_{10}	46.0	42.1	3.9
			Mean...	+ 4.0

* The only notable exception is acrolein, a substance which, as is well known, is difficult to obtain in a state of purity.

SUBSTANCES WITH THREE CARBON DOUBLE BINDINGS.

I.	II.	III. $P\left(\frac{A-1}{d_4^{20}}\right)$	IV. R_A	V. Diff.
Benzole	C_6H_6	42.2	36.9	+ 5.3
Chlorbenzole	C_6H_5Cl	50.7	45.1	5.6
Brombenzole	C_6H_5Br	55.8	50.4	5.4
Aniline	C_6H_7N	49.8	43.5	6.3
Nitrobenzole	$C_6H_5NO_2$	52.6	46.8	5.8
Toluole	C_7H_8	50.1	44.3	5.8
o–Toluidine	C_7H_9N	57.6	51.0	6.6
Benzyl alcohol	C_7H_8O	53.2	47.2	6.0
Mesitylene	C_9H_{12}	65.8	59.2	6.6
Phenylpropyl alcohol	$C_9H_{12}O$	68.8	62.1	6.7
Hydrocinnamic acid ester	$C_{11}H_{14}O_2$	83.3	77.3	6.0
			Mean...	+ 6.0

As may be seen, the molecular refraction of valerylene and diallyl is about 4 units higher than the sum of the atomic refractions R_A —that is to say:

In the case of substances containing two carbon double bindings, the excess of the actual over the theoretical molecular refraction is twice as great as in the case of substances containing but one pair of doubly bound carbon atoms.

$$M_A = P\left(\frac{A-1}{d_4^{20}}\right) = R_A + 4.$$

In the second compartment of the table, we find the difference between the observed and the calculated molecular refraction to be, in the mean, + 6. The deviations from the mean are, however, somewhat greater here than with bodies with but one or two doubly bound carbon atoms, and greater than could have been caused by errors of experiment. This considerable deviation is due to the fact that the benzole derivatives have a large dispersive capacity. The simple Cauchy's formula, with two constants, that was quite sufficient with substances of not too great refractive capacity, is here inadequate for the complete expression of the dispersion, and it is, therefore, not possible, with the aid of this formula, to determine with perfect accuracy the index of refraction, A, for light of infinite wave-length, in the case of the aromatic compounds. Nevertheless, the variations of the differences from the mean is even here not so great as to conceal the relations previously noted. On the contrary, it follows, from the behavior of the benzole derivatives, that:

Substances containing three carbon double bindings, show an excess of the actual over the calculated molecular refraction, which

amounts to three times that resulting from the influence of a single carbon double binding.

$$M_A = P\left(\frac{A-1}{d\,\frac{20}{4}}\right) = R_A + 6.$$

I have already convinced myself of the fact that the molecular refraction increases with the number of the C=C groups. This is, for instance, the case with the derivatives of cinnamic acid, with methyldiphenylamine, etc. The dispersion of these, and all very strongly refractive substances, is so great, that Cauchy's formula, with *two* constants, for the determination of the index of refraction, A, independently of the wave-lengths, is here no longer applicable. I shall, therefore, be obliged to defer the communication of the results obtained with this material until the completion of the somewhat voluminous calculations, made with the aid of a dispersion formula better in accord with the results of the observations. It is, however, even now, hardly to be doubted that the rule which has, so far, proven to be without exceptions, will also prove to be of general application. The rule, namely, that:

The molecular refraction of substances containing carbon double bindings, is greater than the value calculated from the sum of the atoms, and, especially, the excess is proportioned to the number of such multiple attractions; it amounts to 2 units for one, and 2.z for z double bindings.

$$M_A = P\left(\frac{A-1}{d\,\frac{20}{4}}\right) = R_A + 2.z.$$

We have learned from the preceding statements that the molecular refraction increases by two units for each double carbon binding. The atomic refraction of the carbon in saturated compounds is 4,86; we have, therefore, as the equivalent of refraction of the group C=C:

$$C{=}C = 2.4{,}86 + 2 = 11{,}72.$$

As the attraction of the atoms is reciprocal, each of the carbon atoms in the above group contributes in the same measure with the other to the increase of the molecular refraction. The atomic refraction of a single doubly bound carbon atom is, therefore:

$$C{=} \quad = \frac{11{,}72}{2} = 5{,}86.$$

The atomic refraction of carbon increases, therefore, through the double binding, from 4,86 to 5,86, or to the extent of about 20 per cent. of its original value.

From the facts here communicated, it results: *that the atomic refraction of carbon is not invariable, but that it, on the contrary, varies according to the demands upon the valence of the carbon atom. This has been proven to be the case with oxygen, and it most probably holds true of all the polyvalent elements. The atomic refraction of the univalent elements, whose combining capacity is always completely utilized, must, therefore, be constant, no matter with what atoms they are combined.*

This result is furthermore confirmed by the fact, that in the so-called saturated compounds, in which, consequently, all of the available affinity is utilized, the molecular refraction is independent of the mode of grouping of the atoms, and is determined solely by the combining proportions of the elements.

The chemical constitution of bodies is, therefore, only under certain clearly defined conditions, of essential influence on their optical properties—namely, only then when the available affinity of the atoms of the compound in question does not appear to be entirely utilized. The molecular refraction of such bodies may, however, be determined, *a priori*, if the arrangement of the atoms is known.

The molecular refraction is, then, the sum of the atomic refractions, under employment of the specific refraction peculiar to each atom in the condition in which it is bound in the molecule.

If C′ *represents the singly bound carbon atoms, and* C″ *those that are doubly bound to each other, then the molecular refraction of a substance consisting of carbon and hydrogen,* $C'_xC''_yH_w$, *results from the sum:*

$$M_A = P\left(\frac{A-1}{d^{\frac{20}{4}}}\right) = 4{,}86x + 5{,}86y + 1{,}29w.$$

This law may also be expressed in another, and, for practical employment in calculation, more convenient way, thus:

The molecular refraction of the saturated compounds is independent of the mode of grouping of the atoms; it is, namely, the sum of the atomic refractions:

$$M_A = P\left(\frac{A-1}{d^{\frac{20}{4}}}\right) = 4{,}86C_x + 1{,}29H_w = R_A.$$

The molecular refraction of unsaturated bodies is greater than the value calculated from the sum of the atoms, when in such bodies double bindings of the carbon atoms occur, and, especially, the excess amounts to 2 *units for one and* 2.*z for z double bindings:*

$$M_A = P\left(\frac{A-1}{d^{\frac{20}{4}}}\right) = R_A + 2.z.$$

When the analogies were first discovered, which pointed to the optical influence of the multiple bindings of the polyvalent, and especially of the carbon atoms, as the cause of the apparently abnormally high molecular refraction of the so-called unsaturated bodies, the supposition seemed probable that substances containing the acetylene group would show a behavior similar to that of the other unsaturated compounds—namely, that through the elimination of the two hydrogen atoms in the group $-CH=CH-$ of the allyl derivatives, the molecular refraction of the products would again increase. I was, therefore, not a little surprised to learn, through experimental investigation, that the removal of the hydrogen produces an entirely different optical effect.

The known derivatives of acetylene are unfortunately neither very numerous nor even, on account of the marked predisposition of these bodies to polymerisation, very easy to prepare in a state of purity and in larger quantities. I must, therefore, restrict myself at present to the communication of the results obtained in the investigation of the propargyl derivatives. Mr. Louis Henry, who has most obligingly aided me in my work, had the kindness to place at my disposal three representatives of this remarkable class of bodies. The observations made on these three substances are given in the following table:

I.	II.	III. $P\left(\frac{A-1}{d^{\frac{20}{4}}}\right)$	IV. R_A	V. Diff.
Propargyl alcohol.....	C_3H_4O	24.0	22.6	+ 1.4
Propargyl-ethyl ether.....	C_5H_8O	39.5	37.5	2.0
Propargyl acetate.....	$C_5H_6O_2$	39.7	37.8	1.9
				Mean...+ 1.8

As may be seen from column V., the difference between the actual and the theoretical molecular refraction, attains in but one case the previously found mean value for the equivalent of refraction of the double carbon binding.

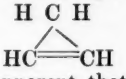
The excess of the observed over the theoretical molecular refraction in the case of the propargyl derivatives, amounts in the mean to 1.8:

$$M_A = P\left(\frac{A-1}{d^{\frac{20}{4}}}\right) = R_A + 1.8.$$

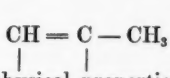
On account of the limited number of the materials for experiment, this expression cannot be claimed to be absolutely exact, and it is, therefore, at present, only to be termed a tolerably close approximation to the truth.

The molecular refraction of the propargyl derivatives is, therefore, greater than that computed from their empirical formulæ. It is, however, remarkable that the elimination of four hydrogen atoms from the corresponding saturated bodies has, in this case, exerted no greater optical influence than a single double carbon binding.

For the present, and as long as more numerous materials for observation are not at hand, the question whether a triple carbon binding is possible or not must remain in abeyance. The optical behavior of the propargyl derivatives would speak against the presence of such binding in these bodies. Their molecular refraction, $M_A = R_A + 1.8$, would be more in accord with the hypothesis of a ring-shaped arrangement of the atoms, or, perhaps, also with that of free valences, so that propargyl hydride, or allylene, would possess one of the following constitution formulæ:



or



It is apparent that the study of the physical properties is precisely adapted to solve such questions as to the arrangement of the atoms.

In a hydrocarbon of the formula, $(C_nH_{2n+2}) - 4H$, the chemical constitution may, for instance, differ, inasmuch as there may occur therein:

1. Two ring-shaped bindings.
2. One ring-shaped and one double binding.
3. Two double bindings.

The molecular refraction gives us information as to which of the different constitution formulæ is applicable, for in each case the optical behavior is different, and especially, the molecular refraction would be:

1. $M_A = R_A$
2. $M_A = R_A + 2$
3. $M_A = R_A + 4$

In a later paper, I shall have occasion to show how, in fact, the molecular refraction may be used to determine the grouping of the atoms in bodies in which it has hitherto been doubtful or altogether unknown.

In the case of saturated compounds, in which the molecular refraction can give no clue as to the arrangement of the atoms, other physical constants may be employed, and the demonstration of these relations will form the subject of a communication in the near future.

AACHEN, November, 1879.

Laboratory of the Royal Technical University.

Abstracts from American and Foreign Journals.

Bulletin de la Société Chimique de Paris.

Abstractor, E. H. S. BAILEY, PH.B.

On the Explosion of a Platinum Retort used for the Concentration of Sulphuric Acid, F. KUHLMANN, JR. (**33**, 50).—The theory of the explosion, supported also by experiment, is that if a small quantity of acid remained in the bottom of the retort, and if water was added and heat gradually applied, there would be a time when the acid would suddenly combine with the water, and heat enough would be generated in this combination to produce the disastrous results described.

Action of Acetic Anhydride upon some Aldehyde-phenols, PH. BARBIER (**33**, 52).—The phenylic aldehydes are capable of giving rise to three kinds of acetic ether derivatives:

1. Those derived from the aldehyde function or part, and which have the formula, $C_{2n}H_{2m}(H_2O_2)O_2,C_8H_6O_6$, and act like a monatomic phenol.

2. Those resulting from the etherification of the phenol part, having the formula, $C_{3n}H_{2m}(C_4H_4O_4)(O_2)$, and the properties of a monatomic aldehyde.

3. Those resulting from a combination of the two previous processes, which have the formula, $C_{2n}H_{2m}(C_4H_4O_4)(O_2,C_8H_6O_6)$, and the properties of an ether.

Those of the second variety, only, can give the coumarins, as previously announced. If salicylal and acetic anhydride be heated in a sealed tube, at 180° for six hours, and the resulting product be distilled, that portion of the distillate coming over at 250–260° is acetosalicylal. In a similar way are made the aldehydes, acetylparaoxybenzoic, acetyloxytoluic (solid) and acetyloxytoluic (liquid). When acetic anhydride acts upon the aldehyde, the reaction is the following: $C_{14}H_4(H_2O_2)(O_2[-] + 2C_8H_6O_6 = C_{14}H_4(C_4H_4O_4)(O_2,C_8H_6O_6) + C_4H_4O_4$. If the product from the above sealed tube be treated with a moderately dilute solution of caustic potash, the ether of the phenol part is attacked, giving: $C_{14}H_4(C_4H_4O_4)(O_2,C_8H_6O_6) + KHO_2 = C_4H_3KO_4 + C_{14}H_4(H_2O_2)(O_2,C_8H_6O_6)$ or diacetic salicylal. If, however, the product be distilled, the ether of the aldehyde is decomposed, and a product of the second variety results:

$$C_{14}H_4(C_4H_4O_4)(O_2,C_8H_6O_6) = C_8H_6O_6 + C_{14}H_4(C_4H_4O_4)(O_2,[-]).$$

On Isophtalophenone, E. ADOR (**33**, 56).—From a study of the salts, the author concludes that the same reaction does not take place in the case of chloroisophtalic acid, as in the case of chlorophtalic acid, when acted upon with benzole. It is not the oxygen which is replaced by two phenyl groups, but the two atoms of chlorine are successively eliminated. The two reactions are

$$C_6H_4(COCl)_2 + C_6H_6 = C_6H_4\begin{cases}COC_6H_5\\COCl\end{cases} + HCl.$$

$$C_6H_4\begin{cases}COC_6H_5\\COCl\end{cases} + C_6H_6 = C_6H_4\begin{cases}COC_6H_5\\COC_6H_5\end{cases} + HCl.$$

If, in place of giving to the phtalic chloride the symbol

$$C_6H_7\begin{cases}COCl\\COCl\end{cases}$$

as suggested by M. Baeyer, we substituted the expression

$$C_6H_4\begin{cases}CCl_2\\CO\end{cases}O$$

the facts observed by him would be readily explained.

On the Reversion of Phosphates in the Superphosphates used as Fertilizers, A. MILLOT (**33**, 98).—In a previous article, it has been noted that those phosphates which became insoluble in the process of manufacture, were phosphates of iron and alumina. Only in case the quantity of acid was not sufficient, did the reverted phosphate contain bicalcic phosphate. If chalk be acted upon by concentrated phosphoric acid, the outside of the grains is changed to bicalcic phosphate; then comes a layer of tricalcic phosphate, and the interior consists of carbonate of lime, unchanged. The reversion noticed in the part soluble in citrate of ammonia, seems to be due exclusively to the action of phosphoric acid and acid calcic phosphate upon sesquioxide of iron, with the formation in the latter case of bicalcic phosphate. In a moist sample, where oxide of iron is present, even in a strongly acid medium, basic phosphates of iron are formed, which are not soluble in citrate of ammonia.

On the Composition of Slate, E. J. MAUMENÉ (**33**, 101).—Slates are usually classified as silicates of alumina, iron and magnesia, free from carbonates. This composition would not explain the action of acids and of atmospheric agents upon them. One specimen analyzed contained over 50 per cent. calcic carbonate. Many others—some of them of excellent quality—contained small

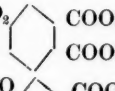
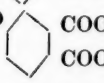
quantities. The presence of calcic carbonate must have a marked effect upon the quality of the slates. The specimen mentioned above had a fine appearance, and was susceptible of high polish, but was readily attacked by acids and atmospheric agents.

On the Determination of Urea by the Alkaline Hypochlorites and Hypobromites, A. FAUCONNIER (**33**, 102).—Noticed elsewhere.

Influence of Sugar upon the Determination of Urea in Urine, M. JAY (**33**, 105).—Noticed elsewhere.

On Active Methylpropylcarbinol and Various Fungi which Destroy it, J. A. LE BEL (**33**, 106).

The α and β Positions in Naphthalene, F. REVERDIN and E. NOELTING (**33**, 107).—Since, by the oxidation of nitronaphthalene an α derivative has been obtained—namely, ordinary nitrophthalic acid:

I. ; and the other isomere corresponding to oxyphthalic acid has been discovered, viz.: II.  , and because oxyphthalic acid has the formula:  , nitrophthalic acid, fusing at 165°, must correspond to the formula II., and the one fusing at 212° to the formula I. The latter is obtained, as has been noted, by means of nitronaphthalene, an α derivative; hence, the α position is that in which the common carbon atoms are contiguous.

On the Volumetric Determination of Active Oxygen in Baric Binoxide and in Oxygenated Water, A. BERTRAND (**33**, 148).—Noticed elsewhere.

On the Artificial Production of Crystallized Arseniate of Iron, A. VERNEUIL and L. BOURGEOIS (**33**, 151).—To make artificial scorodite ($Fe_2O_3As_2O_5 + 4H_2O$), iron wire is treated, in a sealed tube, with a conc. (50 per cent.) solution of arsenic acid, at 150°, for several days. An abundant coating of gelatinous matter at first forms on the wire; this gradually, however, disappears, with the formation of scorodite. The mass is then treated with conc. solution of ammonia, which dissolves out the excess of arsenious acid. The substance obtained is identical with scorodite in specific gravity, specific heat, percentage composition, and crystalline form.

On the Reversion of Phosphates soluble in Citrate of Ammonia, A. COLSON (**33**, 153).—Bicalcic phosphate is not always soluble in citrate of ammonia. For instance, if an acid phosphate of lime be concentrated at a temperature of about 60°, phosphoric acid and bicalcic phosphate, containing an excess of water, are formed. This phosphate only partially dissolves in citrate of ammonia, even upon prolonged standing. Time may also be an important factor in diminishing the solubility of the bicalcic phosphate in citrate of ammonia. In some superphosphates there is a very rapid reversion, so that a loss of soluble phosphates amounting to 10 or 15 per cent. takes place in a few hours. Since a large quantity of sulphuric acid is used in the manufacture of many fertilizers, this reversion cannot be due to double decomposition, or to the action of unattacked oxides. It is possible that the free snlphuric acid, or that combined with iron and alumina, may act on the lime of the phosphate, and form sulphate of lime, which, taking away water from the phosphates, modifies their composition, and renders them largely insoluble in citrate of ammonia. Experiments seem to prove this to be the case.

Preparation of Pure Levulose, C. GIRARD (**33**, 154).—The sugar is first inverted by adding 20 c.c. HCl per kilogram of sugar, and heating to 60°. Slaked lime is then added, in excess, and the pasty mass is repeatedly pressed, to separate liquid glucosate of calcium from the solid levulosate. After suspending the latter in water, the lime is exactly precipitated by oxalic acid, and upon cooling (by means of ice and hydrochloric acid), most of the water crystallizes out of the filtrate, and the resulting levulose is completely dried in a vacuum.

Note upon the Reactions produced by Solution of Dimethylamine upon various Metallic Solutions, C. VINCENT (**33**, 156).

On the Properties of Bicalcic Phosphate, A. MILLOT (**33**, 194).—Bicalcic phosphate, containing five molecules of water, dissolves readily in ammoniacal citrate of ammonia. The phosphate with only one equivalent of water, dissolves much more slowly. Bicalcic phosphate loses its water of crystallization and is decomposed, in boiling water. If the phosphate is mixed with water, and gradually brought to the boiling point, the solution becomes acid, acid phosphate of lime is dissolved, and the residue consists of a mixture of bi- and tricalcic phosphates. If boiling solutions of phosphate of soda, chloride of calcium, and acetic acid are mixed together, bicalcic phosphate, with one equivalent of water, is obtained; this, however, is mixed with a little tricalcic phosphate. If this reaction takes place in the cold, a bicalcic phosphate is obtained, containing five equivalents of water.

Journal fuer Praktische Chemie.

Abstractor, EDGAR EVERHART, PH.D.

On the Desulphurization of Guanidine Thiocyanate, SIEGMUND BYK (**20,** 328).—The author has attempted to obtain a substituted cyanguanidine by treating guanidine thiocyanate with various metallic oxides. The results were always negative, whether he treated the thiocyanate in alcoholic or in aqueous solution, or whether he heated it in sealed tubes. No desulphurization took place. The oxides of mercury and lead, in an alcoholic solution, have but little action on the thiocyanate, except to produce a slight decomposition into ammonia and carbonic acid. Oxide of mercury produces a precipitate in the aqueous solution, which the author regards as a compound of mercuric thiocyanate with guanidine thiocyanate and mercuric oxide, although it could not be prepared in a pure condition. On boiling with acetic acid, in which it is soluble, it yields guanidine thiocyanate and $C_2H_3O,HgCNS$; on boiling with concentrated hydrochloric acid, the double salt, $CN_3H_5,HCL + 2HgCl_2$, is obtained.

When the guanidine thiocyanate, however, is treated with metals or metallic oxides, when molten, a quite different reaction takes place, and a partial desulphurizing is brought about. When, for instance, plumbic oxide or finely divided lead is added to melted guanidine thiocyanate, plumbic sulphide and a body, having the formula, $C_7H_{15}N_{13}O$, which the author calls cyanmelamidine, are obtained. Hydrochloric or sulphuric acid, as well as potassium permanganate, decomposes the substance into melamine, $C_3H_6N_6$, nitric acid into ammeline and hydrocyanic acid.

On Ethylenechlorosulphocyanide and β Chlorethylsulphonic Acid, WILLIAM JAMES (**20,** 351).—By warming, on the water-bath, a mixture of ethelene chlorobromide with potassium thiocyanate, the author obtains the ethylene chlorosulphocyanide, $C_2H_4,Cl(SCN)$, as a colorless liquid, boiling at 202–203°, and having a smell something like mustard oil. The oil is highly refractive, very miscible with alcohol and ether, and does not solidify at —20°. When the foregoing substance is treated with fuming nitric acid, it is oxidized to chlorethylsulphonic acid, $CH_2ClCH_2SO_3H$. The barium salt crystallizes with $2H_2O$, in needle-shaped crystals, grouped in stellate forms. Its silver salt, when heated with ammonia to 100–120°, yields taurine.

Chemical Analysis of the "Ferdinandsbrunn Quelle," at Marienbad, in Bohemia, W. F. GINTL (**20,** 356).

On the Compounds of Lithium Chloride and Magnesium Chlorides with Alcohols, S. E. SIMON (**20,** 371).—The author prepares the compounds by dissolving the chlorides in absolute alcohol. All are very deliquescent. Lithium unites with ethyl alcohol, forming colorless, shining, deliquescent crystals, having an astringent taste, like lithium chloride. The formula for the ethyl alcoholate is $LiCl + 4C_2H_6O$. The other salts prepared were $LiCl + 3CH_4O$, $MgCl_2 + 6C_2H_6O$ and $MgCl_2 + 6CH_4O$.

Electrolytic Experiments, E. DRECHSEL (**20,** 378).—The author gives a preliminary article on the decomposition of substances by the galvanic current, when the direction of the current is quickly changed by a self-acting commutator. The substance first used in his experiments was ordinary ammonic carbonate. Two platinum electrodes were dipped in the solution, and the commutator allowed to work with great rapidity for ten hours. There was no perceptible elevation of temperature. On evaporating the solution, a crystalline salt, containing 64.7 per cent. of platinum was obtained. Hydrochloric acid gives a light green, nitric acid a cerulean blue precipitate from its aqueous solution. When the galvanic current was allowed to act on the solution of $(NH_4)_2CO_3$, without changing its direction, there was a great elevation of temperature, and, on evaporating the solution, no platinum salt was found. On slowly changing the direction of the current, the temperature rose, but, on keeping the solution cool, from the outside, a platinum salt was obtained, having 38.6 per cent. of platinum. The author also describes another experiment, in which he used a solution of grape sugar, containing some sodic phosphate. Two large platinum electrodes, separated by a piece of filter paper, were dipped in the solution, and, after electrolysis, the platinum was found covered with brownish leaves, which, on burning, left decided traces of platinum.

On some Derivatives of Propionic Acid, B. FREYTAG (**20,** 380).—When thiocarbamide is heated in sealed tubes to 100°, with monochlorpropionic acid ether, a crystalline salt of the hydrochlorate of lactylthiocarbamide = $CS\begin{cases}NH-C_2H_4\\ \quad\quad |\\ NH-CO\end{cases}$. HCl, is produced. With platinic chloride, it gives a double salt, which is decomposed by water into lactylthiocarbamide and hydrochloric acid.

On warming, on the water-bath, propionic acid anhydride with thiocarbamide, the solution, when cold, solidifies to a crystalline mass,

which has the composition of propionylthiocarbamide. When chlorpropionic acid ether is heated to 150–160°, with potassium thiocyanate, thiopropionic acid ether is produced, $CH_3,CH(SCN).CO_2.C_2H_5$.

Reply to Mr. Peter Classon, on the Action of Sulphuryl chloride on the Alcohols, PAUL BEHREND (**20**, 382).

On the Decomposition of Albuminoids in Pumpkin Seeds, E. SCHULZE and J. BARBIERI (**20**, 385).—*Ber. der d. chem. Gesell.* (**11**, 210, 1233).

On the Behavior of Arsenical Bismuth with Nitric Acid, and the Preparation of Basic Bismuthic Nitrate free from Arsenic, R. SCHNEIDER (**20**, 418).—The author finds that, when bismuth containing arsenic, is broken into lumps, and gradually added to five times its weight of nitric acid, and heated to 75–90°, the bismuth is dissolved, forming bismuthic nitrate, absolutely free from arsenic, the latter element forming an insoluble arsenate of bismuth. The bismuthic nitrate may be freed from the arsenate by allowing the liquid to stand for several days, and then decanting and filtrating. The filtrate, on evaporation, yields crystals of bismuthic nitrate, which may be converted into the basic salt by ordinary means.

On the Possibility of the Existence of Fungoid Growth in an Atmosphere free from Oxygen, J. W. GUNNING (**20**, 434).—A reply to M. Nencki (*vide Journ. fuer pr. Chem.*, **19**, 337, and this JOURNAL, **1**, 494).

On the Chemical Composition of Bacteria, M. NENCKI and F. SCHAFFER (**20**, 443).—The authors found that, when a liquid containing bacteria was boiled for a few minutes with an acid, as hydrochloric, sulphuric or acetic, the bacteria were precipitated as a white, compact mass, that can be easily filtered and washed. As no fluid precipitated by boiling could be used for propagating the growth of the bacteria, gelatine was chosen as the proper medium. After washing with alcohol, the bacteria were exhausted with ether. The etherial extract, which greatly resembles fat, gave 72.54 per cent. C., and 11.73 per cent. H. The bacteria themselves contain about 84 per cent. of water; dried, from 6 to 7.9 per cent. fat, 3.25 to 5.03 per cent. ash, and 84 to 86 per cent. of albuminates, which, in turn, are composed of 53.07 to 53.82 per cent. carbon, 7.09 to 7.82 per cent. hydrogen, and from 13.82 to 14.34 per cent. nitrogen. The bacteria, after exhaustion with ether, dissolve almost completely in weak alkaline solutions, without the disengagement of either ammonia or sulphuretted hydrogen. This solution, after filtration and

saturation with hydrochloric acid, on the addition of a concentrated solution of salt, deposited a white, flocky precipitate, which has the composition, 52.37 per cent. carbon, 7.88 per cent hydrogen and 13.60 per cent. nitrogen. The authors call the new albuminoid mycoprotein. It has the same composition as the albuminoid substance of beer yeast, prepared in the same way. As sulphur was proven to be absent, it agrees well with the formula, $C_{25}H_{42}N_6O_9$. When freshly precipitated, it is easily soluble in water, acids and the alkalies, but, after drying at 110°, it is no longer completely soluble in water. Its reaction is feebly acid. It is lævo-rotary; acids convert it into peptone; with an alkaline copper solution, it gives a violet color.

The residue, insoluble in dilute alkali, consists of cell membrane, containing a little nitrogen, which may, however, have come from some unacted-on albumen.

The Empirical Formula of Skatole, M. NENCKI (**20,** 466).—Pure skatole, the production of which follows that of indole in the process of putrefaction, was obtained by allowing pancreas and muscle to putrefy for the space of five months. After acidifying with acetic acid, the mass was subjected to distillation. The skatole which distils off with the water, was acidified with hydrochloric acid, and precipitated with picric acid. On distilling the picric acid compound with ammoniacal water, and crystallizing the distillate from hot water, the pure skatole was prepared. The formula was found to be C_9H_9N.

On Carbamido-palladious Chloride, E. DRECHSEL (**20,** 469).—When either aqueous or acid solutions of palladium chloride and urea are mixed together, a brownish-yellow crystalline compound is formed, having the composition $2CH_4N_2O.PdCl_2$. As this compound is but very slightly soluble in water, and almost insoluble in alcohol, the author tried to use it for the separation and quantitative estimation of urea, but without success, on account of the incomplete precipitation. Palladium, however, can be completely precipitated from its solutions. By heating with an excess of water, this compound is gradually decomposed into palladio-ammonium chloride, $PdCl_2.2NH_3$, and palladio-diammonium chloride, $PdCl.4NH_3$. When evaporated with an excess of $PdCl_2$, it is decomposed into $PdCl_2.4NH_3$, with the formation of biuret, which, the author thinks, is produced by some free cyanic acid being formed, and entering into combination with urea. The author further attempted to form hydantoic acid by the action of carbamido-palladious chloride on glycerine, but

without success. The products obtained by the reaction were biuret, urea hydrochloride, palladium bases, and palladium amidoacetate.

On the Source of Hippuric Acid in the Urine of Herbivorae, O. LOEW (**20**, 476).—The author, in a former paper, has described the discovery of an acid in meadow hay, closely resembling quinic acid. He has not, however, been able to prepare it in a pure condition, owing to its admixture with a peptone-like substance. The acid shows the more important reactions of quinic acid.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office,** by ARNO BEHR.

March 2, 1880.

225,108.—*Coloring matter obtained from alpha-naphthol.* HEINRICH CARO.

The coloring matter is dinitroalphanaphthol-sulphoacid, and is obtained by the action of nitric acid upon alpha-naphthol-sulphoacid.

225,119.—*Glue cement.* JOHN FIRMBACH.

1 lb. of glue, 2½ oz. bichromate of potassium, ¼ oz. permanganate of potassium.

225,133.—*Slating compound, for erasable tablets.* HENRY W. HOLLY.

The compound consists of water-glass, oxide of zinc and silicate of magnesium.

March 9, 1880.

225,261.—*Composition of matter for making moulded articles of manufacture.* ORATOR F. WOODWARD.

"Gypsum and rosin mixed together under heat."

225,279.—*Preparation of bank-note paper.* HENRY HAYWARD.

225,282.—*Process of treating paper for detective purposes.* NAPOLEON T. HECKMANN.

The details of this and the preceding patent must be looked for in the specifications.

225,300.—*Manufacture of aluminous cake.* CARL V. PETRAEUS.

White aluminous cake is manufactured from aluminous sulphate containing iron, by treating the aluminous sulphate, in solution, with alkaline sulphides.

225,301.—*Manufacture of aluminous cake.* CARL V. PETRAEUS.

In order to reduce the peroxide of iron contained in crude sulphate of alumina, the solution of the latter is boiled with finely divided lead. This is either spongy lead, precipitated from a solution by some metal, or lead powder, obtained by blowing steam into melted lead.

225,356.—*Preparation of metallic lead.* ASAHEL K. EATON.

For use in the manufacture of white lead, as packing for stuffing boxes, etc. Lead is prepared in the form of hair or thread-like fibre. For process see specification.

225,400.—*Fluid soap.* ELISHA W. LINCOLN.

Water, lye, borax, ammonia, alum, soda, coal-oil, and a little tallow.

March 16, 1880.

225,518.—*Composition for preserving eggs.* ADAM GOOD.

The eggs are dipped in a hot solution of borax, sugar and lime, and then dried.

225,658.—*Composition for grinding wheels.* CHARLES E. STEVENS.

Consists of emery, silicate of soda, carbonate of lime and oxide of manganese.

225,679.—*Plastic compound.* ARTHUR T. WOODWARD.

This compound is suitable for insulating telegraph wires under ground or water, and for coating other metal articles. It consists of 90 per cent. of ground glass and 10 per cent of pulverized resin, either with or without an admixture of a drying oil.

March 23, 1880.

225,697.—*Insecticide compound.* JNO. E. GIBSON.

A mixture of tar, paris green, sulphur and saltpetre, is applied to the bark, in order to destroy the borer.

225,730.—*Manufacture of nitrogen gas.* THOMAS B. STILLMAN.

In order to obtain nitrogen free of oxygen, the gas is passed through melted sodium contained in a closed vessel.

225,772.—*Process for finishing leather.* MOSES B. TICE.

A complicated process, the particulars of which must be seen in the specification.

225,817.—*Composition for filling teeth.* THOMAS FLETCHER.

The principal ingredients are pyrophosphate of alumina and phosphoric acid.

225,858.—*Manufacture of non-inflammable paper.* CHARLES H. O'CONNOR.

The paper, wholly or partially unsized, is saturated with a solution of silicate of soda, and dried.

225,908.—*Artificial coloring matter.* FRANCOIS Z. ROUSSIN.

Claims the coloring matters produced by the action of diazonaphtalin-sulpho acid on the amines, amides and phenols.

March 30, 1880.

225,977.—*Manufacture of nickel-zinc alloy.* THEODOR FLEITMANN.

The alloy is produced by reducing a mixture of the oxides of nickel and zinc, and rapidly melting the metal.

225,991.—*Compound for artificial stone.* ARCHIBALD K. LEE.

226,017.—*India-rubber and other gum compounds, for surfacing cloth and for other purposes.* CHARLES Y. BEACH.

The smell of india-rubber is covered by an admixture with it of gumbenzoin.

226,057.—*Process for the treatment of india-rubber.* HENRY GERNER.

The process consists in grinding the india-rubber in a "frozen" state.

226,058.—*Manufacture of goods from caoutchouc.* HENRY GERNER.

Claims a composition of equal parts of camphor, sulphur and caoutchouc.

226,070.—*Treating waste vulcanized caoutchouc.* LUDWIG HEYER.

Claim 1. The process of regenerating waste caoutchouc consisting of subjecting it to the direct action of heat, in connection with the vapor of heated water.

2. The process of regenerating waste caoutchouc by subjecting it, after the removal of the sulphur by the direct action of heat, to the action of boiling water or steam, and then straining it.

226,136.—*Process for preserving meats.* HENRY WARDEN.

The pickling fluid is injected into the veins of the carcass, and afterwards air, or an oxidizing gas, is injected in the same manner, in order to expel the pickling fluid.

226,143.—*Dephosphorizing iron in the puddling process.* WM. A. O. WUTH.

In order to prevent the re-absorption by the iron of the phosphorus contained in the slag, the latter is drawn off, and replaced by a charge of slag practically free of phosphorus. In this slag, the iron is heated higher, and the operation finished.

Foreign Patents.

Condensed from R. BIEDERMANN'S Report to the German Chemical Society, by OTTO H. KRAUSE.

FRED. PAUR, Montbéliard: *Desulphurization of pyrites residues.* (Germ. P., No. 8730, May 22, 1879.)—The residues are boiled with a solution of potassium permanganate. Potassium sulphate and manganic peroxide are formed. The former is removed by washing; the latter remains with the ferric oxide, and may be used for the same purposes as manganiferous iron ore.

ORAZIO LUGO, Flushing, New York: *Purification of gas.* (Engl. P., No. 1410, April 9, 1879.)—Illuminating gas mixed, according to the amount of impurities present, with 0.8 to 2.9 per cent. by volume, of air, is purified by contact with animal charcoal impregnated with tar. The air added is supposed to decompose the hydrogen sulphide, and the nitrogen is supposed to form ammonia under the influence of the animal charcoal.

J. SPOONER HOWARD, F. G. BATES and F. P. PENDLETON, Philadelphia: *Manufacture of aluminium and aluminium alloys.* (Engl. P., No. 1909, April 17, 1879.)—The inventors claim to prepare aluminium by simply heating a mixture of 1 lb. precipitated alumina, 1 oz. of coal and 3 oz. sodium chloride, in a crucible to 700° F., and aluminium alloys by merely stirring alumina into a molten metal, copper, for instance. (R. Biedermann thinks it is a pity that these inventors did not demonstrate long ago to Messrs. Woehler and Ste. Clair Deville, what a simple thing it is to prepare aluminium.)

(See also this JOURNAL, **1**, 408.)

JEAN MARIE HARMET, Lyons: *Dephosphorization of iron in two operations.* (Germ. P., No. 8949, March 20, 1879.)—Silicium and carbon are removed from the fused iron contained in a Bessemer converter, having an acid lining. The iron separated from the slag is then run into a second converter, having a basic lining, and there dephosphorized. The composition of the linings is not stated.

FRED. THOM. READE, London: *Dephosphorization of iron.* (Engl. P., No. 1877, April 22, 1879.)—Pulverized limestone is blown together with the air through the metal contained in a Bessemer converter.

A. G. GREBEL, Paris: *Process of enameling cast iron.* (Engl. P., No. 1183, March 22, 1879.)—The finely pulverized enamel is applied, with suitable precautions, to the inner surface of the mould. The heat of the molten metal fuses the enamel into the surface of the iron.

DUGALD CLERK and C. A. FAWSITT, Glasgow: *Coating iron and steel with platinum.* (Engl. P., No. 1182, March 25. 1879.)—Platinum foil is applied to malleable iron or steel at a welding heat.

E. W. PARNELL, Liverpool: *Manufacture of zinc paint.* (Engl. P., No. 549, February 12, 1879.)—Precipitates an alkaline solution of oxide of zinc with an alkaline sulphide, and proposes to remove sulphides from crude soda lyes by adding alkaline solution of zinc, and so obtain sulphide of zinc as a by-product.

JOHN CAWLEY, Deptford: *Manufacture of zinc sulphide.* (Engl. P., No. 1047, March 17, 1879.)

TH. GRIFFITHS, Birkenhead: *Manufacture of zinc sulphide.* (Engl. P., No. 1131.)—Both patents are essentially the same as Germ. P., No. 8138, of March 29, 1879, to Griffiths and Cawley. See this JOURNAL, 1, 588.

G. MCROBERTS, Glasgow: *Explosive compound.* (Engl. P., No. 1090, March 19, 1879.)—The inventor adds cotton, infusorial earth, sawdust, pulverized charcoal, or other absorbent non-explosive matters, to Nobel's mixture of nitroglycerine and gun cotton, or methyl-nitrate and gun cotton.

JOHN WATSON, Gateshead: *Manufacture of Portland cement.* (Engl. P., No. 1510, April 17, 1879.)—Mixes 2 parts blast furnace slag, 5 parts lime and 2 parts clay, and calcines and grinds the mixture.

A. C. A. HOLTZAPFEL, Newcastle: *Coating for ships' bottoms, etc.* (Eng. P., No. 1028, March 15, 1879.)—Mixture of tar, wood spirit, rosin, shellac, turpentine, oxides of iron and mercury, sulphide of antimony and arsenic.

J. LEVINSTEIN, Manchester: *Preparation of orange and scarlet coloring matters.* (Engl. P., No. 623, February 15, 1879.)—The orange coloring matters obtained by the action of α or β-naphtholsulphonic acid upon diazobenzole or its homologues, are separable by digestion with ammoniacal wood spirit or alcohol into a scarlet coloring matter which is insoluble, and an orange dye which can be obtained by evaporating the solution.

P. POULIN, Chaulnes, France: *Separation of woolen and cotton fibres.* (Engl. P., No. 1512, April 18, 1879.)—The cotton is removed by boiling the stuff in a solution of calcium chloride at 20° Bé, or in a solution of sodium chloride acidified with hydrochloric acid. (Neither method is new.—R. B.)

C. STIERLIN, Paris: *Artificial leather.* (Germ. P., No. 9140, June 13, 1879.)—Carded cotton is put into a bath composed of glue 25 parts, water 75 parts, clay 20 parts, and tannin 5 to 10 parts, wrung out and tanned during 12 to 24 hours in a decoction of oak bark containing 5 per cent. of glycerine.

HUGO ALISCH, Berlin: *Syphon for acids.* (Germ. P., No. 9133, October 14, 1879.)—A receiving vessel, from which a glass tube passes into the carboy, is placed over the latter. By means of a three-way cock, the vessel can be connected with an air-pump or opened to the air. The acid is aspirated into the upper vessel, from which it may be drawn off as wanted, a ball valve preventing its return to the carboy.

W. MUELLER, Antwerp, and E. GEISENBERGER, Brussels: *Improvements in the manufacture of ammonia.* (Engl. P., No. 1481, April 16, 1879.)—Barium or potassium nitrate or nitrite is heated in a retort, and the gaseous products of the decomposition passed together with steam into a second retort, containing coal heated to redness, and in which the liberated hydrogen and nitrogen combine, forming ammonia.

The base remaining in the first retort is reconverted into nitrate or nitrite, by bringing it into contact with oxygen and nitrogen under the influence of electricity. According to another patent of the same inventors (Engl. P., No. 1592, April 22, 1879), ammonia may be prepared from hydrogen and atmospheric nitrogen, under the influence of electricity, in the following manner: Steam is passed through retorts containing coal heated to redness, and the hydrogen gas pumped into a reservoir to be cooled and purified. The gases from the furnace which heats the retorts are drawn, by means of a pump, into another recep-

tacle in which lime absorbs the carbonic acid. The gases from both receivers are then passed into a mixing vessel; a glass tube near the lower end contains the wires between which the electric sparks are made to pass. The ammonia formed is absorbed in the ordinary manner.

H. UJHELY, Vienna: *Purification of ozokerite.* (Engl. P., No. 333, January 17, 1879.)—Instead of treating ozokerite with steam, sulphuric acid and bone black, to prepare paraffine and ceresine from it (see Grabowsky, *Wagn. Jahresber.*, 1877, 1039), the inventor dissolves it in the light hydrocarbons from petroleum or tar, or in bisulphide of carbon. The solution is filtered through bone black, and the purified ozokerite obtained by evaporation in vacuo, distillation, or exposure to a low temperature.

J. J. SACHS, Barrow, Furness: *Extraction of greasy matters from textile fabrics.* (Engl. P., No. 1673, April 29, 1879.)—The goods are treated with solution of sodium silicate. Neither the process nor the apparatus employed contain novel features.

J. RADIG, Schweidnitz: *Odorless fertilizing powder* (Germ. P., No. 8466, June 17, 1879.)—Calcined sodium sulphate, dried kieserite and ferrous sulphate are added to human excreta.

A. NOBEL, Paris: *Explosive compound.* (Engl. P., No. 226, January 20, 1879.)—Explosive bodies, of rapid and tardy explosibility, are mingled in such proportions as to produce a mixture having the desired degree of explosibility.

HULENZ and DREYFUSS, Paris: *Process of waterproofing textile fabrics, leather, &c.* (Engl. P., No. 438, Feb. 3, 1879.)—By employing a mixture composed of 1000 parts white wax, 60 varnish, 40 Burgundy pitch, 80 peanut oil, 50 ferrous sulphate, and 20 essence of thyme.

MATTHIS and WEBER, Duisburg. *Apparatus for continuously concentrating liquids by steam.* (Germ. P., No. 8464, May 30, 1879.)—Cannot be properly described without the drawing. The liquid to be evaporated is made to pass in an opposite direction to steam, in a multi-tubular apparatus.

A. RUEMPLER, Hecklingen: *Process and apparatus for recovering magnesia from the magnesian scum obtained in defecating beet juice.* (Germ. P., No. 9144, September 14, 1879.)—The scum is calcined in inclined, closed cylinders, open below. The ammoniacal vapors given off are condensed in a vessel filled with moist lumps of unburnt gypsum or kieserite.

THOMAS ATKINS, Clapham: *Manufacture and purification of illuminating gas.* (Germ. P., No. 9280, April 25, 1879.)—Two retorts are placed, the one within the other. "Compound gas" is evolved from a mixture of bones, shale and coal, contained in the inner retort, which is perforated, and mixes with the coal gas generated in the outer retort, increasing its illuminating power. The residue remaining in the retort, is mixed in layers with lime, and employed in the purification of the gas.

THE AMERICAN CHEMICAL SOCIETY.

XVI.—Proceedings.

Regular Meeting, April 1, 1880.

Thirteen members present. Dr. E. R. Squibb in the chair.

The minutes of the previous meeting were read and approved.

In the absence of a quorum the regular business was deferred.

The following papers were read.

1. "Miscellaneous Chemical Notes," by T. T. Morrell. 2. "On Peroxide of Hydrogen and Ozone" (second paper), by Prof. A. R. Leeds.

After which the meeting adjourned.

ARTHUR H. ELLIOTT,

Recording Secretary.

XVII.—Miscellaneous Chemical Notes.

By T. T. Morrell.

I. ESTIMATION OF SMALL QUANTITIES OF POTASH WITH PLATINIC CHLORIDE.

When an aqueous solution of platinic chloride is mixed with potassium iodide, there is produced a peculiar red coloration of remarkable intensity, according to the reaction:

$$PtCl_4 + 6KI = K_2PtI_6 + 4\ KCl.$$

Advantage may be taken of this reaction to estimate, colorimetrically, minute quantities of platinum, providing no other substance, which produces with the iodide a colored solution, is present. If a solution of platinic chloride of known strength is kept on hand, a standard for measuring the color may be formed by mixing a measured quantity with potassium iodide.

An excess of pure iodide appears to have no effect upon the intensity of the color. However, it is best to use about the same quantity in the estimation and in the formation of the standard color, allowing five or six minutes to develop the maximum tint, after which the solutions may be suitably diluted. It is well, also, to keep the cylinders in which the comparison of color is made, stoppered, to exclude the air as much as possible.

To apply this test to the estimation of the small quantities of potash found in lime-stones, clays, etc., the double salt with platinic chloride is formed, and washed upon the filter as usual. The filter is put in a warm place, until most of the alcohol or ether, used in washing, has evaporated, when the precipitate may be dissolved in a little hot water. The solution is now cooled, and transferred to the testing cylinder, and iodide is added. If the iodide is added in crystals, it is best to agitate the liquid while it is being dissolved, to prevent the solution at the bottom of the cylinder from becoming too concentrated.

Instead of estimating colorimetrically, we may, since two equivalents of iodine would be yielded to reducing agents, titrate the solution with chloride of tin. For this purpose, a little hydrochloric acid is added, and the tin solution is run in until the red color disappears, and the solution is pale yellow. The end of the reaction is sharply defined, if the amount of the platinic salt is not too great. The addition of hydrochloric acid deepens the color, but always in proportion to the platinic salt present.

II. ESTIMATION OF COPPER AS OXIDE.

When copper has been precipitated as sulphide, it is sometimes ignited with a little flour of sulphur, in a stream of hydrogen, and weighed.

I have sometimes resorted to a shorter and equally accurate method, which I do not remember to have seen in print, viz.: that of converting the sulphide directly into oxide. For this purpose, the sulphide is removed from the filter, the filter ash added, and the whole roasted for a short time at a gentle heat. It is now very carefully heated, several times, with a little nitrate of ammonia, by which it is converted into oxide free from every trace of sulphuric acid.

If fuming nitric acid is at hand, the sulphide may be warmed with a few drops, and the resulting mixed oxide and sulphate ignited, two or three times, with a little powdered carbonate of ammonia, and weighed. This is easier of execution than the ignition with nitrate of ammonia, as the latter is apt to deflagrate, if the heat is not very carefully applied.

III. COMPOSITION OF THE GASES IN THE CAVITIES OF A BESSEMER INGOT.

In December, 1876, I made an analysis of the gases contained in the "blow-holes" of a Bessemer ingot. The ingot was "bottom cast," eight ingot moulds being simultaneously filled from a central

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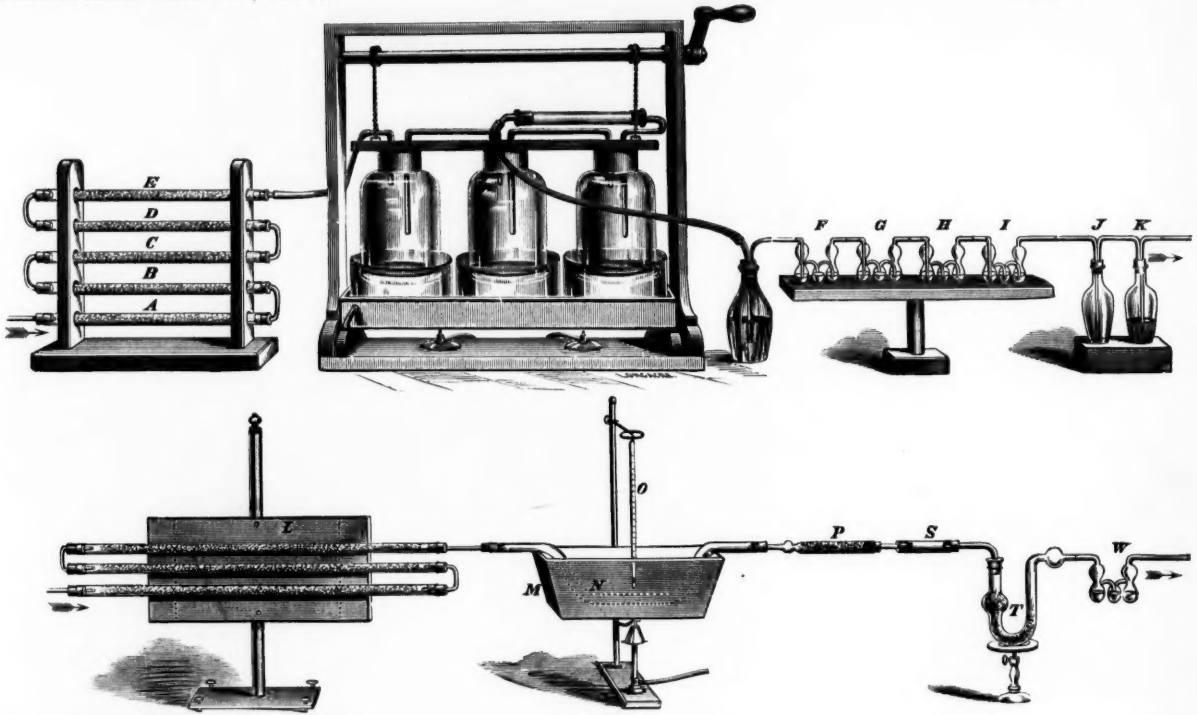
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sprue, down which considerable air was carried along with the metal. The result of the analysis leaves little doubt that the bottom, made of red bricks and fire-clay, was not thoroughly dry. The gases were collected over water, the ingot being immersed in an iron box, with a drill passing through a packing box into its side. The boring was done as rapidly as possible. This method of collecting the gases is not free from objections, but was the best at command. The average of two closely accordant analyses was as follows :

Carbonic oxide	2.08
Hydrogen	56.42
Nitrogen	39.36
Oxygen	2.14

A few of the cavities near the surface evidently communicated with the air, hence a little free oxygen, and a larger percentage of nitrogen.

The specific gravity of the solid steel, about one foot from the top of the ingot, was 7.866.

XVIII.—On Peroxide of Hydrogen and Ozone.

By Albert R. Leeds, Ph.D.

[Second Paper.]

(*With Figures on Plate I.*)

Read April 1st, 1880.

I.—Upon the relative amounts of peroxide of hydrogen and ozone, obtained in the ozonation of air by moist phosphorus, as determined by the method of decomposition of these bodies, through the agency of heat.

In preceding articles, and more especially in the first paper with the above title, it has been pointed out that both hydrogen peroxide and ozone are formed by the action of air upon moist phosphorus. Moreover, a number of experiments, protracted for several months (in which as many as 481 liters of purified air were used in a single experiment, and every devisable precaution was employed), were brought forward in support of the proposition that *the percentage of hydrogen peroxide in the ozonised air bears a constant ratio to that of the ozone.* The conclusion drawn from these results was, that the production of hydrogen peroxide, like that of ammonium nitrate, depends upon the same series of chemical changes as those which are

concerned, in this instance, in the generation of ozone itself. Moreover, that the connection between the production of the three bodies is a necessary one, and that any hypothesis which explains the generation of the ozone, and ignores the contemporaneous generation of hydrogen peroxide and ammonium nitrate, is of necessity imperfect, and, to a certain extent, erroneous.

The object of the present article is to demonstrate by a method entirely different from that previously employed :

I. That both hydrogen peroxide and ozone are generated by the action of air upon moist phosphorus.

II. That after very prolonged contact with one another, in a series of wash-bottles and dessicating tubes, both bodies survive in amounts capable of satisfactory estimation.

III. That when the current of ozonised air, containing hydrogen peroxide, is passed through a tube heated to various temperatures, the amount of water obtained by the decomposition of the hydrogen peroxide increases with the increment of temperature.

IV. That under these circumstances, the amount of the residual gas capable of decomposing a neutral solution of potassium iodide, regularly diminishes, and at 200° no such decomposition whatsoever occurs.

V. That after this point has been attained, if a solution of potassium iodide (entirely free from iodate) which has previously been acidified with sulphuric acid, be substituted for the neutral solution, it will undergo slow decomposition. This result is due, not to ozone, which is completely destroyed by continued exposure to a temperature of 200°, but to the spontaneous decomposition of an acidified solution of potassium iodide in presence of oxygen.

The objects kept prominently in view, in devising the method of the experiment, were :

1st. To bring filtered and purified air in contact with a large surface of phosphorus, the phosphorus being partly immersed in distilled water, quite free from ammoniacal and nitrous compounds, and maintained during the course of the experiment, at the temperature of maximum evolution of ozone (24–25° C.)

2d. To wash out of the ozonised air, as large an amount of hydrogen peroxide as possible, by an extended series of wash-bottles.

3d. To free the ozonised air, after its escape from the wash-bottles, from every trace of moisture.

4th. To decompose the hydrogen peroxide and ozone, at gradually increasing temperatures.

5th. To weigh any water, and to titrate any ozone, remaining after the ozonised air had been subjected to the action of heat.

These ideas were embodied in the arrangement of apparatus represented in the accompanying drawing (see Plate I). The train of purifiers, A, B, C, D, E, of which A was filled with the "absorbent hygroscopic cotton" (prepared according to von Bruhns), B and C, with glass beads drenched with soda solution, D and E, with sulphuric acid, was connected with the "phosphorus ozonator." The water in the jars of the ozonator was maintained throughout the course of all the experiments at 24–25° C. The ozonator was connected with a wash-bottle by means of kerite tubing, and the wash-bottle to four Geissler bulbs, F, G, H and I, the entire five being partly filled with water. The last bulb was connected with an empty wash-bottle, J, and this again with a wash-bottle, K, containing sulphuric acid. The drying was completed by three drying tubes, L, filled with beads drenched with sulphuric acid.

The entire length of these driers was $2\frac{1}{2}$ meters.

From the driers, the ozonised air passed into a curved glass tube, N, dipping down into an oil-bath, M. The middle portion of this tube for a length of 0.25 meter, was filled with amianthus, which had previously been ignited. The object of this amianthus filling, was to cause the ozonised air to filter through a great extent of heated air passages. After this followed a weighed sulphuric acid drying tube, P, a sulphuric acid guard tube, T, and a Geissler bulb containing a neutral solution of potassium iodide, W. Between P and T, an empty tube, S, closed with corks at both ends, was interposed, for convenience in slipping out the drying tube, P. All the connections were made either with strips of cotton cloth, bound tightly about the tubes with flower-wire and coated with melted paraffine applied with a brush, or by corks boiled in paraffine.

A number of preliminary experiments were tried, in order to determine whether on aspirating air only through the apparatus, the weighed drying tube, P, would change weight, or the potassium iodide solution would undergo decomposition. The former was found to be the case, a result attributed to the failure to detain all the moisture contained in the air before its reaching the tube, P. In these experiments, instead of the three drying tubes figured at L, but one was employed, having a length of 0.85 m. It was therefore supplemented by two more tubes, filled with phosphoric anhydride, and having together a length of 1.75 m.

This arrangement answered perfectly, so far as the detention of moisture was concerned, the drying tube, P, not altering in weight in repeated trials, when air alone was drawn through the apparatus. The oil-bath was then raised to a temperature of 200°, and the ozonator thrown into action. Six liters of air were drawn through the apparatus at this temperature, and six more at 150°. No change occurred in the potassium iodide solution in both experiments. This did not excite surprise, inasmuch as the complete decomposition at these temperatures of any ozone which might be present, was highly probable. But on repeating the trials, upon the same amounts of air at 100° and 22°, it was found, most unexpectedly, that the iodide solution did not change. There was no question as to the destruction of the ozone, during the course of its passage through the apparatus, inasmuch as it was plentifully evolved by the ozonator. Three ways of accounting for this decomposition were probable. Either the ozone was destroyed by the slow action of the hydrogen peroxide, generated simultaneously by the action of moist air upon phosphorus, or it was expended in acting upon the paraffine connections; or it was decomposed by the phosphoric anhydride. Since the arrangement of the apparatus differed only by the introduction of phosphoric anhydride from many similar arrangements hitherto employed in experimenting upon ozone, the last supposition appeared the one most probable.

On examining the anhydride, it was found to contain no uncombined phosphorus, but a notable amount of phosphorous anhydride, the raising of which to the highest stage of oxidation, had been the cause of the entire disappearance of the ozone.

The phosphoric anhydride in the drying tubes was therefore replaced by sulphuric acid, when it was found that the irregularities above noticed entirely disappeared.

Paraffine does not perfectly withstand the action of ozone, being slowly decomposed, with the formation of carbonic acid. In the course of long continued use, the paraffine joints employed by the author in connecting the ozonising elements of his large electrical ozoniser (JOURNAL AMER. CHEM. SOC., I, 440), were destroyed, and had to be renewed from time to time. The amount of action on the joints was progressive, the paraffine connection between the first and second ozonising element requiring to be changed very seldom, while that between the eleventh and twelfth elements needed frequent removal. This increase of action demonstrated the effect of prolonging the time during which the same portion of oxygen was subjected to the influence of the silent discharge. In experimenting with

ozonised air, containing so small an amount of ozone as that employed in the investigation described in the present article, the connections may be made of paraffine without entailing serious error, but in researches of greater nicety, where not merely the relative but the absolute amounts of ozone have to be determined, paraffine connections cannot be employed.

The following experiments were performed under as nearly as possible identical conditions. Twelve liters of ozonised air were drawn through the apparatus in each experiment, at the rate of six liters per hour. The ozonator was maintained at the temperature of 24° C. The increase in weight of the drying tube, P, corresponded to the water formed by the decomposition of the hydrogen peroxide, when heated to the temperatures indicated in the table. The amounts of iodine set free in the potassium iodide solution are calculated into ozone according to the equations :

$$2KI + O_3 + 2HCl = 2KCl + I_2 + H_2O + O_2 \text{ and}$$
$$2KIO_3 + 2HCl = 2KCl + I_2 + O_2 + H_2O,$$

each molecule of ozone corresponding to two atoms of iodine. A large number of trials were made without throwing the ozonator into action, and it was only when the sulphuric acid drier, P, both at 0° and when the oil-bath was heated to 200°, became constant in weight, that the experiments recorded in the table were performed.

Table showing the relative amounts of hydrogen peroxide and ozone formed during the ozonation of air by moist phosphorus:

	Experiment.	Temperature.	Water.	H_2O_2	Ozone.
1st Series.	I.	100°	0.0015 grm	0.0028 grm	Not determ.
	II.	50°	0.0010 "	0.0019 "	"
	III.	24°	0.0000 "	0.0000 "	"
2nd Series.	IV.	200°	0.0010 "	0.0019 "	0.0000 grm
	V.	200°	0.0011 "	0.0020 "	0.0000 "
	VI.	150°	0.0002 "	0.0004 "	0.0011 "
3rd Series.	VII.	100°	0.0015 "	0.0028 "	0.0013 "
	VIII.	50°	0.0003 "	0.0006 "	0.0044 "
	IX.	21°	0.0000 "	0.0000 "	0.0037 "
4th Series.	X.	200°	0.0018 "	0.0034 "	0.0000 "
	XI.	100°	0.0002 "	0.0004 "	0.0011 "
	XII.	22°	0.0000 "	0.0000 "	0.0051 "

These experiments, it appears to us, establish the truth of the first, second and fourth propositions. They show that *both* hydrogen peroxide and ozone are formed, and that on heating the ozonised air, the proportion of water thus produced regularly increases, while that of the ozone diminishes, until at 200° all the hydrogen peroxide is converted into water, and all the ozone into ordinary oxygen. At the close of the twelfth experiment, the immediate train of driers,

etc., was thrown out, and the Geissler bulb containing the potassium iodide solution, was connected directly with the first wash-bottle (that preceding F). The same volume of ozonised air, at the same rate, being drawn over under these conditions, gave a result corresponding to 7.94 mgrm, instead of 5.1 mgrm, as in experiment XII. In both experiments, the temperature of the ozonator was 24°, and of the iodide solution, 22°. The difference of 2.84 mgrm, which is 36 per cent. of the amount of ozone originally evolved, represents the loss due to the decomposition effected by the simultaneous presence of hydrogen peroxide.

This establishes the second proposition, and shows not only that peroxide of hydrogen and ozone can co-esist for a long time, in dilute condition, without great loss of either, but also that the amount of hydrogen peroxide in the ozonised gas, bears a not inconsiderable proportion to that of the ozone itself. In fact, neglecting the small amounts of hydrogen peroxide, which later on are shown to have been held back in the wash-water, the ratio of the hydrogen peroxide to the ozone exceeds one to three.

To determine the truth or falsity of proposition V.—"That the air, after being deprived of its hydrogen peroxide and ozone, could bring about a decomposition of an acidified solution of potassium iodide," the experiment was again repeated with the tube N, maintained at a temperature of 200°. It will be noted that in every preceding trial at this temperature, a *neutral* solution of the iodide being used, *no liberation of iodine* occurred; but in this experiment, a decomposition took place corresponding to 0.21 mgrm of ozone. The increase in weight of the sulphuric acid drying tube, P, due to the decomposition of hydrogen peroxide, and the fixation of water, was 0.0022 grm. This experiment proves that the oxygen contained in a current of air, from which every trace of hydrogen peroxide and of ozone, has previously been removed by strong heating, may produce apparently the ozone reaction, *in case the potassium iodide solution used for titration has been acidified.*

It may be objected, although the objection is not supported by the above results, that even after passing through an amianthus plug 0.25 m. in length, maintained at the temperature of 200°, all the hydrogen peroxide had not been decomposed, and the residual peroxide had brought about the change noted. It may also be said that the result had been due to the use of potassium iodide, containing iodate. To show that a far simpler supposition accounts for the decomposition, the experiment was performed with air alone, and po-

tassium iodide, from which every trace of iodate had been removed, was used. To prepare by the method we have found most convenient* any amount of the crystallized iodide, absolutely free from traces of iodate, is so troublesome, that we preferred to employ a salt containing iodate, but from which the iodate had been carefully removed before using. This we attempted to do by throwing down the iodic acid with baryta, and then getting rid of the excess of baryta from the boiling solution by means of carbonic acid. But a notable amount of barytic iodate remained in solution. It was found better to saturate the neutral solution of potassium iodide, containing iodate, with hydrosulphuric acid, and then drive off the last traces of H_2S by heating. With this precaution, the potassium iodide sold as chemically pure, may be used in investigations similar to the foregoing.

20 c.c. of such a potassium iodide solution, containing 10 per cent. of iodide, was placed in one Geissler bulb, and the same amount slightly acidified, in another bulb, the two being connected together, and $4\frac{1}{2}$ liters of air drawn through them. At the expiration of $1\frac{1}{2}$ hours, the *neutral* solution was entirely *colorless;* the *acidified* solution contained 4.4 *mgrms of free iodine.*

This experiment points out too emphatically to need any comment, the magnitude of the error brought about by the use of acidified solutions in various titrations, and especially where it is used to estimate the ozone contained in a slowly moving current of ozonised air.

II.—AMOUNT OF HYDROGEN PEROXIDE ABSORBED BY THE WASH-WATERS.

In earlier experiments, undertaken first, to determine the relation between the temperature and volume of the ozone given off by the action of moist phosphorus upon air, and second, to estimate the amounts of by-products, the quantities of hydrogen peroxide had been determined in the wash-water only. This was done, after testing with metadiamidobenzole had established the absence of nitrous acid. In one series of experiments, the hydrogen peroxide thus determined, was the $\frac{1}{100}$th part of the total weight of ozone evolved. Moreover, only the wash-water in the first wash-bottle was titrated, inasmuch as that in the bottles placed later in the series, contained too little hydrogen peroxide to permit of satisfactory estimation. But it was found by these later experiments, that this method gave *a much too low result for the relative percentage of hydrogen peroxide,* since the greater part of it was not held back by the wash-water.

*Contributions to the Chemistry of the Atmosphere, Ann. N.Y. Acad. Sci., 1

The bulb F, containing 47 c.c. of water, after evaporation to two-thirds its original volume, in order to expel any dissolved ozone, was found to contain 0.2 mgrm H_2O_2. The bulb G, containing 26 c.c. of water, after being similarly evaporated, gave a reaction corresponding to 0.08 mgrm H_2O_2. The bulb H, to 0.01 mgrm H_2O_2. The falling off in the amount of hydrogen peroxide contained in F, in comparison with that in G, is perhaps greater than should be, for the reason that H and I were changed during the course of the experiments, and a much smaller volume of ozonised air passed through them, than through the two preceding bulbs. But the striking feature in the experiment is, that only 0.3 mgrm of H_2O_2 in all was absorbed by the wash-waters, the remainder passing on in the stream of ozonised air.

III.—UPON THE RELATIVE AMOUNTS OF HYDROGEN PEROXIDE AND OZONE.

The considerations above detailed, render manifest that the solution of this problem is attended with great difficulties. For the titration must be effected either in the neutral or acid solution of potassium iodide. In case the former is employed, there is no reason for supposing that any of the ozone itself escapes without decomposition. The statements which have been made to the contrary, have probably been based on the fact, that the potassium iodide solution has been employed to absorb a mixture of ozone and of hydrogen peroxide held in aerial suspension. And, moreover, the observation of von Babo has been lost sight of, that whenever ozone is decomposed by potassium iodide solution, hydrogen peroxide is set free. But the case is different with the hydrogen peroxide present in the ozonised gas. A very small portion of this undergoes absorption by a neutral solution of potassium iodide, as is strikingly shown by the following experiment. A Geissler bulb containing an 0.8 p er cent solution of hydrogen peroxide, was connected with another bulb filled with a 10 per cent. solution of neutral potassium iodide, and 12 liters of air were aspirated through the two bulbs, the current flowing from the former through the latter. If the current of air merely decomposed a portion of the peroxide into water and free oxygen, no iodine would be liberated, inasmuch as oxygen alone is without action upon pure neutral potassium iodide. But, if any H_2O_2 were vaporised and carried over, it might be expected to act, although not energetically, upon the neutral solution. This latter supposition was the one which accorded best with the results of the experiment. The first bulb of the

Geissler apparatus became decidedly, the second bulb slightly, yellow. On titration, it was found that 0.02 mgrm of H_2O_2 had been absorbed.

What would occur if the titration of the ozonised gas were performed in an acidified solution of potassium iodide? In the first place, a decomposition would result from the action of the air alone, which would vitiate the results. In the second place, even an acid solution acts very slowly upon hydrogen peroxide, when the latter is present in extremely small amount. Thus, Schoene* has shown that it is only in somewhat concentrated solutions that the decomposition is complete after a short period. In a solution which contained in 1 liter nearly 1 grm H_2O_2, 24 hours were required for the completion of the reaction. When about one-quarter grm H_2O_2, in a liter, was present, it was not until after 30 hours that 98.2 per cent. of the total amount of hydrogen peroxide had been decomposed. With greater dilution, still less action ensued, and with only 5 mgrms H_2O_2 to the liter, after 48 hours, less than three-quarters of this amount had been decomposed.

IV.—PRODUCTION OF HYDROGEN PEROXIDE, DURING THE DECOMPOSITION OF POTASSIUM IODIDE BY OZONE, AND THE ORIGIN OF THE WHITE CLOUD FORMERLY THOUGHT TO INDICATE THE PRESENCE OF ANTOZONE.

One of the most singular phenomena connected with the action of moist phosphorus upon air, is the dense white cloud which makes its appearance *after* the ozonised air has issued from the potassium iodide solution. If this cloud is drawn over into an aspirator bottle, it gradually disappears on standing. The phenomena are of such a character that it is difficult to avoid framing the hypothesis, that we have to deal, not with one, but with two substances, one of which is absorbed by the potassium iodide solution, while the other passes on, and asserts itself by the production, in contact with water, of this mysterious white cloud. In fact, the hypothesis of the dual nature of active oxygen, the ozone and atmizone of Meissner, the ozone and antozone of Schoenbein, had come to be regarded as well established, and has only recently been overthrown. The credit of so doing is generally assigned to Nasse and Engler, who demonstrated that the so-called antozone, is merely hydrogen peroxide, diffused through a large quantity of aqueous vapor.† But this merit rather belongs, it

* Zeitschr. fuer analyt. Chemie, **18**, 145.

† Ann. der Chim. und Pharm., **154**, 230.

seems to me, to von Babo,* since his work hardly appears to have obtained the consideration which it deserves, and since some of his most important conclusions are, even at the present time, generally overlooked by writers upon this subject. I think it will be well to re-state them here. He says, "the formation of the cloud is always to be noted, when in any manner whatsoever ozone is decomposed, water being present. The clouds occur in the greatest intensity, when a portion of the ozone escapes decomposition, and this portion, as Meissner has quite correctly observed, acts in the dry condition upon the aqueous solution, in which it produces oxidation.

"Meissner believes that the clouds are not hydrogen peroxide, because this is not volatile, and therefore are due to a peculiar modification of oxygen (antozone).

"When ozonised oxygen acts upon oxidizable bodies, a reaction occurs for which we have many analogies. For instance, in the oxidation of a substance, not only is this body acted upon by the oxidizing agent, but in some instances, the operation of this agent extends to other bodies, which otherwise are not attacked. It may suffice to instance the oxidation of nitrogen in the burning of ammonia, or the solution of platinum, alloyed with silver, in nitric acid. Even so, ozone by itself does not act upon water, but oxidizes it when, at the same time, it acts upon other readily oxidizable bodies.

"In like manner, by its action upon potassium iodide, together with free iodine, potassium peroxide and potassium iodate, *hydrogen peroxide is formed.*" (The italics are the authors.) "When a dry current of ozone goes through a solution containing potassium iodide, the dry gas readily takes up vapor of water, which diffuses itself in the gaseous current, and thus, at least in part, becomes saturated with water vapor. By the action of the ozone, on the one hand, iodine is made free, and on the other hand, the vapor of water is oxidized. Along with these, a volatile combination of iodine and ozone may be formed. The formation of the hydrogen peroxide may be brought about by the oxidation of the fluid as well as of the gaseous water.

"Since, however, the hydrogen peroxide can only exist in the fluid condition, the portion which is formed in the gas condenses no fog vesicles, that is to say, a liquid suspended in the gas. This can swim for some time in the gas without decomposition, inasmuch as it finds itself in an atmosphere more or less saturated with water vapor, the

* Beitr. zur Kentniss des Ozons, Ann. der Chem., Suppl. 1 and 2, 1863, 290.

reason of the rapid decomposition (the abstraction of water) not being present. How far such a cloud can be conducted through an apparatus, how difficultly condensible it is, is not surprising, when one reflects on the well-known behavior of other solid or fluid bodies suspended in gases. The destruction of the cloud, the so-called '*abklingen*' of the atmizone, can happen in part through the gradual precipitation of the hydrogen peroxide, and in part through its decomposition, as when, for example, the gas is not sufficiently saturated with water vapor."

We believe that the theory advanced by von Babo is the correct one, and that it affords a satisfactory explanation of the phenomena associated with ozonation, whether the method by phosphorus, or by electrolysis, or by the silent discharge, be employed.

For when in the ozonation by phosphorus, the white clouds (of phosphoric anhydride and peroxide of hydrogen) which at first accompany the evolved gas, are completely absorbed by repeated washing with water, they make their appearance again *at the moment when* the ozone is decomposed by a potassium iodide solution. The phenomenon is a very striking one. The de-ozonised air, laden with the suspended hydrogen peroxide, thus generated, will present the appearance of a white cloud for a long time, even when absorption of the peroxide is slowly taking place at the surface of the water in the vessel into which the air has been aspirated.

Still more convincing are the phenomena attendant upon the ozonation by the silent discharge. To study these with more care, the following experiment was performed: perfectly pure and dry oxygen was ozonised by one of the "ozonising elements" (see JOURNAL AMER. CHEM. SOC., **1**, 441), and then drawn through three bulbs, the first containing solution of neutral potassium iodide, the second water, and the third chromic acid. The latter was connected with an aspirator. As soon as the strongly ozonised oxygen came into contact with the potassium iodide, a very slow current being employed, a yellow coloration made its appearance on the surface of the solution in the *first bulb*, and above the surface the characteristic white cloud. On increasing the rapidity of the current, this white cloud was drawn through the water and chromic acid, into the aspirator, and remained for one or more hours before its absorption was complete. After drawing over 6 liters of oxygen, containing 0.194 mgrm of ozone, the water was titrated, and found to have absorbed 0.31 mgrm of peroxide of hydrogen. The chromic acid solution was unaffected, showing that the suspended hydrogen peroxide may pass

through it without effecting a decomposition. The same remark applies to a neutral potassium iodide solution, put in the place of the chromic acid. The excessively dilute hydrogen peroxide held in a state of aerial aqueous suspension, was not able to decompose the neutral iodide during the course of the experiment. Of course, an *acidified* solution could not be employed to absorb the peroxide, since, as above shown, its decomposition occurs under the action of oxygen alone.

A final series of experiments was then tried with the following objects:

1st. To repeat the experiment of Andrews (R. Soc. Proc., **7**, 475; Ann. der Chem. u. Pharm., **97**, 371), and to determine whether the amount of ozone, as determined by titration, was precisely the same as that determined by weighing, with suitable precautions, the potassium iodide solution used for absorption, before and after the experiment. Also, to discover if possible, the sources of the anomalies observed by Andrews, when a neutral solution of iodide was employed.

2d. To establish whether, the same volume of oxygen being employed in two experiments performed under otherwise identical conditions, the amount of ozone as determined by the titration and weighing of an acidified solution of potassium iodide, would not be in excess of the amount as determined by the titration and weighing of a neutral solution.

3d. After drying the oxygen, on its leaving the potassium iodide solution, to find the amount of hydrogen peroxide, generated by the decomposition of the ozone in presence of water, and of an oxidizable body.

4th. To discover the alterations in composition which the potassium iodide solution, itself, had undergone; to find out what proportion of the potash set free by the liberation of the iodine, had by a further process of oxidation, been converted into iodate, and in what condition the remainder was left, so that it was without action on the liberated iodine.

To perform these experiments, the apparatus employed above was modified by the introduction of a sulphuric acid drier, after the potassium iodide bulbs, and the drier was again protected by a guard from the latter part of the train. Before attaching the apparatus, similar to that shown in the wood-cut, for determining the hydrogen peroxide evolved from the potassium iodide bulb, the experiments included under the first head were performed:

First, with neutral solution of iodide.

The weights of the solution and the drier were carefully determined, before and after each experiment.

Amount of ozone, as found by increment of weight.	0.114 grm.
" " " titration.....	0.108 "
Excess (as determined by weighing).....	0.006 "

2.75 liters of oxygen were drawn over in 2 hours and 40 minutes.

Repeated.

Amount of ozone, as found by increment of weight.	0.0972 grm.
" " " titration.....	0.0804 "
Excess (as determined by weighing).....	0.0168 "

2.75 liters of oxygen were drawn over in 3 hours.

Second, with acidified solution of potassium iodide.

Amount of ozone, as found by increment of weight.	0.0768 grm.
" " " titration.....	0.0798 "
Deficiency (as determed by weighing).....	0.0030 "

3.5 liters of oxygen were drawn over in 3 hours.

Repeated.

Amount of ozone, as found by increment of weight.	0.0942 grm.
" " " titration	0.1062 "
Deficiency (as determined by weighing).....	0.0120 "

3.25 liters of oxygen were drawn over in 3 hours.

The first feature which strikes us in inspecting these results is, that the amounts of ozone as determined by weighing, are in excess when the neutral, and in deficiency when an acid, solution of potassium iodide was employed. This result was one which could have arisen from the presence of carbonic anhydride as an impurity in the ozonised oxygen. On interposing a bulb, containing barytic hydrate, before the iodide solution, the formation of a white precipitate showed that this impurity was actually present. It was not contained in the oxygen used, since this had been most carefully purified, but was formed by the action of the ozone on certain paraffine connections employed. The cause of the deficiency, when an acidified

solution of iodide was employed, is not so plain. Since the error due to the paraffine vitiated the results, the continuation of the experiments has been postponed until an apparatus constructed entirely of glass could be obtained.

But it was very evident that the white cloud formed when an acidified solution was employed in the titration, was more conspicuous than when a neutral solution was used. If we suppose, as von Babo states, that in addition to potassium iodate, potassium peroxide and hydrogen peroxide are formed at the same time, then the reaction in the neutral solution may be represented by the equation:

$$4KI + 2H_2O + 6O_3 = K_2O_2 + 2KIO_3 + I_2 + 3O_2 + 2H_2O_2,$$

and the decomposition of the K_2O_2, according to the equation,

$$K_2O_2 + 2HCl = 2KCl + H_2O_2,$$

would result in additional liberation of hydrogen peroxide from the the acidified solution.

Much has been written concerning the nature of the reaction which ensues when potassium iodide is decomposed by ozone, and the hypothesis of Schoenbein has found favor in some quarters, that while potash is formed and is present in the solution, the liberated iodine is protected from its action by the presence of a large excess of potassium iodide. The objections to this theory are, it appears to me, insuperable. In the first place, no excess of potassium iodide, however large, will prevent the combination of free potash with dissolved iodine. In the next place, if we take a potassium iodide solution which has been decomposed by ozone, and wash out all the liberated iodine by carbon disulphide, the colorless liquid remaining will not have the slightest alkaline reaction. Now, whether this neutral liquid contains potassium iodate alone, or this body, together with potassium peroxide, the result would be the same on the addition of acid; a fresh portion of the potassium iodide would be decomposed, with liberation of iodine. But a quantitative analysis showed that the amount of potassium combined as iodate, was not sufficient to account for all the iodine set free on acidifying. Hence, we believe that the explanation of von Babo is the correct one, and that, in addition to potassium iodate, small amounts of potassium peroxide and hydrogen peroxide are also formed.

XIX.—Review of Berthelot's "Mécanique Chimique."*

By Ch. de Marignac.†

Translated for the Journal of the American Chemical Society, by P. Casamajor.

On witnessing the calorific effects which accompany the act of chemical combination, chemists have at all times sought to determine the relations which exist between these two classes of facts; on the one side, affinity, considered as the cause of all chemical combination; and, on the other side, the heat produced when this combination takes place.

A century ago, Lavoisier explained this relation, by assuming that simple bodies are only known to us in a state of union with a certain quantity of caloric, which is set at liberty when these bodies enter into chemical combinations. Having his attention more exclusively attracted to the phenomena of combustion, he attributed this too exclusively to oxygen. Later, it was admitted for all the elements.

The brilliant discoveries of Davy, on the chemical decompositions effected by the galvanic current, gave rise to the electro-chemical theory, proposed by this scientist, and afterwards adopted and modified by Ampére and Berzelius, which caused heat and affinity to be looked upon in an entirely new light. According to this theory, affinity is merely the reciprocal attraction of the opposite electricities, which exist in either a free, or a polarized state, in the elements which tend to combine, and the heat observed in chemical combinations results from the mutual neutralization of these electricities.

When chemists abandoned the electro-chemical theory, they returned to the system previously adopted, admitting, at the same time, the pre-existence of caloric in all the elements. But, about this time, an important revolution took place in the physical sciences; heat and electricity ceased to be considered as material fluids, combined more or less intimately with ponderable bodies, and came to be regarded as modes of motion. The discoveries of Mayer, of Golding, of Joule, had demonstrated the mechanical equivalent of heat. This new doctrine necessarily modified the ideas entertained by chemists concerning the origin of the heat and the electricity evolved in chemical reactions, and led them to consider these mani-

* Essai de Mécanique Chimique, Fondée sur la Thermo-chemie, par M. Berthelot; Dunod, Editeur, Paris, 1879.

† Published in the Archives des Sciences Physiques et Naturelles, and republished in the Moniteur Scientifique, of February, 1880.

festations as complementary to one another, and as resulting from the loss of molecular impetus attending the act of combination.

Vast erudition, and long bibliographical researches, would be necessary, to follow this change of doctrine, and to apportion to each scientist the share which he had in it. We may, however, cite the memoir of M. Henri Sainte Claire Deville (1860), and those of Babinet (1866).

A Danish chemist, Mr. Thomsen, whose labors have greatly contributed to the progress of thermo-chemistry, published in 1853 a series of memoirs,* in which he explained the principles of this new science. Without deriving them explicitly from the mechanical theory of heat, he expresses the basis on which they rest in terms which recall this theory. He founds them on the two following principles:

1st. The intensity of chemical energy in a given body is constant when the temperature is invariable.

2d. The totality of the heat given out in a chemical reaction, is the measure of the chemical energy brought to bear in this reaction.

The chemical energy of a body, or, what is identical, its capacity of developing heat, is what Mr. Thomsen calls its *thermo-dynamic equivalent.*

Mr. Thomsen has since tried to show that all the laws of thermo-chemistry subsequently established by M. Berthelot, were derived from the second of these principles. It is true that they may be considered as consequences of it, but only by including conditions and restrictions which are not found in the statement of this principle. The best proof of this is that fifteen years later,† when Mr. Thomsen attempted to establish an agreement between his principles and the manner in which bases and acids are divided in a mixture of salts, he had to introduce a new force, *avidity*, which is an inherent property of these bodies, and in which it is difficult to find anything different from chemical affinity under another form, independent of that which is measured by the heat given out in combinations.

It is in reality to M. Berthelot that the honor belongs, of having stated with perfect precision the fundamental principles of thermo-chemistry, and, above all, of having shown, by a prolonged and numerous series of experiments, that these principles are sufficient to account for all chemical reactions.

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*Pogg. Annal., **88**, 349; **90**, 261.

† Pogg. Annal., **136**, 65; also, Archives, 1869. **36**, 301.

Gifted with an eminently philosophical spirit; deeply versed in mathematics and in the physical sciences; trained to the most extended researches by his labors on chemical synthesis, this scientist was better able than any one else to accomplish the task to which he has devoted himself, which is to show the application of the principles of mechanics to the formation of organic compounds, and even to chemical reactions generally.

For this, it was not sufficient merely to determine the heat given out in chemical reactions. A not less important portion of the labors of M. Berthelot has been the study of the conditions under which such reactions take place, and more specially the study of the chemical equilibrium which results from two contrary reactions, which are reciprocally limited. This happens in the formation of ethers, in decompositions and inverse re-combinations produced by electricity, etc.

Through the study of these subjects, the author was led to new and important results in a branch of chemical mechanics, already intimated at the beginning of this century by Berthollet, under the name of *chemical statics*. He has shown that the theory of Berthollet, by which we are enabled to foretell chemical phenomena from the mere knowledge of the physical conditions of insolubility and volatility, has no foundation, except when there already exists a previous equilibrium, which constantly tends to renew itself. But the permanency of this equilibrium, and even its existence, are dependent on a still more general condition, which had never before been pointed out, and which has been defined in the principle of *maximum work* laid down by M. Berthelot.

These researches have taken sixteen years—since 1864. The results have been given in numerous memoirs, published in the *Annales de Chimie et de Physique*. M. Berthelot acknowledges the great help he has had from the labors of his predecessors: Hess, Graham, Andrews, Favre and Silbermann, and in the numerous series of numerical determinations of the quantities of heat given out in combinations, made by Mr. Thomsen, which are generally remarkable for their accuracy.

This subject is not exhausted, and will not be for many years, but M. Berthelot thinks that the time has come for him to state the laws and general principles, the search of which has led him to this long series of experiments, and to show in what manner the ideas recently acquired on the theory of heat, allow us to bring the whole of chemistry, that is, the formation and reactions of organic as well

as of mineral substances, under the same principles of mechanics which govern other branches of physics; whence the title of "*Essay on Chemical Mechanics founded on Thermo-chemistry*," given by the author to the work which we are reviewing.

In his introduction, M. Berthelot states the three fundamental principles of thermo-chemistry and chemical mechanics, viz :

I. PRINCIPLE OF MOLECULAR ACTION.—*The quantity of heat given out in any reaction is the measure of the sum of the physical and chemical work accomplished in this reaction.*

This principle gives the measure of chemical affinities.

II. PRINCIPLE OF THE CALORIFIC EQUIVALENCE OF CHEMICAL TRANSFORMATIONS, or, in other words, PRINCIPLE OF THE INITIAL AND FINAL STATE.—*If a system of simple or compound bodies, taken in determinate conditions, suffers physical or chemical changes capable of bringing it to a new state, without giving rise to a mechanical effect exterior to the system, the quantity of heat given out or absorbed by the effect of these changes, depends solely on the initial and final states of the system ; it is always the same, independently of the nature and sequence of intermediate states.*

III. PRINCIPLE OF MAXIMUM WORK.—*Every chemical change, accomplished without the intervention of a foreign energy, tends toward the production of the body, or system of bodies, which gives out the greatest quantity of heat.*

The prevision of chemical phenomena is, by this last principle, brought down to the purely physical and mechanical idea of the maximum labor accomplished by molecular action.

The following principle, deduced from the preceding, is applicable to a multitude of phenomena :

Every chemical reaction, which may be accomplished without the help of a preliminary action, and apart from the intervention of any energy foreign to the bodies present in the system, will necessarily take place if it be attended with evolution of heat.

The two first principles, above given, had not heretofore been stated in such precise terms, but, it may be said that they had been implicitly admitted by the previous investigators in thermo-chemistry. It was, however, M. Berthelot, who first called attention to the principle of maximum work, which is the basis of chemical statics.

In the statements made above, we may note the particular care taken by the author in distinguishing, in the calculations of re-

actions, the heat given out by chemical reactions, properly so called, from that due to change of state, and which is derived more specially from physical energies, such as the liquefaction of gases, the solidification of liquids, changes of volume and of specific heats of gases, of liquids and solids ; changes of tension in vapors, and of fluidity in liquids, of crystallization and of crystalline form in solids ; also, various modifications of the amorphous state.

It is indeed only on the condition of keeping account of all these circumstances, and of eliminating the share of all these physical causes, that we are able to ascertain that the heat given out in a reaction, is the exact measure of the affinities brought into play.

The first volume of M. Berthelot is specially dedicated to *chemical calorimetry*, which is the study of the quantities of heat given out in chemical reactions. It forms the exposition and confirmation of the first two principles stated above.

These principles cannot be demonstrated *a priori*. They are founded on a hypothesis, in itself very probable, that the imperceptible molecular motions developed in chemical reactions, obey the same laws as the motions of mechanical motors, which may be seen and measured. The accuracy of this hypothesis can only be established by long series of experiments, and by the constant conformity of the results obtained with those foreseen by theory.

The first volume is divided into three books. The first book develops the rules and general methods of chemical calorimetry. The author reviews the various reactions, combinations of elements, formation of salts, &c. He gives the calculations for each case, also gives rules for taking into account all the physical actions which intervene in these reactions, and shows, by numerous examples, the agreement of experience with the fundamental principles established by him.

One chapter is devoted to the quantities of heat which come into play in the reactions which take place in living beings. Another chapter treats of the variation of the heat of combination as influenced by temperature.

The second book contains descriptions of experimental processes and of calorimetric apparatus, for the determination of the quantities of heat given out in chemical reactions, of specific heats, and of the heat due to changes of state.

The great experience of the author gives a special interest to this description of the methods and apparatus used by him, in which he

has succeeded in uniting simplicity with accuracy, and in which he has tried to eliminate or, at least, to reduce as much as possible, the corrections made necessary by the influence of exterior causes.

The third book is devoted to numerical tables. It includes numbers obtained by experiment, representing the quantities of heat given out or absorbed during physical or chemical changes of state which these bodies undergo in the operations of our laboratories. It therefore contains, besides results of thermo-chemical experiments, all the data relating to specific heats, and to changes of state (latent heats). It forms an extensive and exceedingly useful compendium of the labors of all the scientists who have studied these questions. We also find in this portion very interesting discussions on numerous theoretical questions suggested by the examination of these results. We may cite more specially those which relate to specific heat.

M. Berthelot states that the specific heat is the only physical property by which simple gases differ from compound gases. This property, however, is sufficient to establish between these two groups such an important difference, that it is impossible to suppose that any of the gases, now considered as simple, results from the union of several other elements, such as we admit them at the present time, or from the condensation of several equivalents of the same element. This union or condensation must be understood to be comparable to that which gives rise to compound bodies, such as are now known to us. Simple gases differ from all compound gases formed with condensation, by the constancy of their specific heat, while for these last, the specific heat increases rapidly with the temperature, and always exceeds in a notable manner, at all temperatures, that of simple gases. They also differ from compound gases, formed without condensation of their elements, such as hydrochloric acid and carbonic oxide (corresponding to four volumes, according to the system of notation of the author), whose molecular specific heat is equal to that of simple gases, and also remains constant at all temperatures, by the fact that the molecular volume always corresponds to one equivalent for these compound gases, while it represents two or four equivalents for all the known elements.*

* This difference is not so much in the specific heats themselves, as in the relations of molecular volumes to equivalents. In this respect, the reasoning of M. Berthelot does not seem to me unobjectionable. It would be so if the determinations of equivalents rested on fixed rules. But, as he himself acknowledges (Introduction, page 21), "equivalents are only determined within an approximation of a multiple," it would only be necessary to change the multiple which has been chosen more or less arbitrarily, for a given body, to change the

In the chapter relating to specific heats of solid bodies, occur very interesting observations on the law of Dulong and Petit,* and on the relations which exist between the specific heats of compound bodies and those of their elements.

The second volume of the work of M. Berthelot, is specially dedicated to establishing the bases of chemical mechanics.

The object at which the author aims is the highest that science can propose to itself. Instead of confining itself to the individual description of the properties, the preparation and transformations of chemical species, science must endeavor to discover the laws governing these transformations; the causes and proximate conditions which determine them. The complete solution of this problem of chemical mechanics is not yet possible, and will not be possible for many years. To solve it, we should know, in every reaction, the masses of the particles brought into play, their relative positions, the proper motions of each particle, the exact nature, and the laws which govern the forces which react on each other. Most of these data are wanting, and even if they were known, it is doubtful if any method of calculation would allow us to solve such a complicated problem.

However, some portions of the problem may be attempted. Since a long time, all that relates to the proportions in which combinations take place is known by the laws of definite proportions, of multiple proportions, and of equivalents. As to the prevision of reactions, we have only had the laws laid down by Berthollet at the beginning of this century. These only apply to special cases and meet with frequent exceptions. M. Berthelot replaces them by a more general law, by which the prevision of the reciprocal actions between simple and compound bodies is reduced to the determination

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relation between its molecular weight and its equivalent, which the author regards as characteristic of simple and compound gases. As an instance, it is not clear why M. Berthelot considers the molecule of carbonic oxide, C_2O_2 (four volumes), as representing one equivalent. In the combinations of this gas with oxygen, chlorine and sulphur, it would appear that this quantity rather corresponds to two equivalents.

* Although we acknowledge, with M. Berthelot, that the law of Dulong and Petit, when applied to solids, is not rigorously exact, and that it cannot serve, in an absolute manner, for the determination of atomic weights, still we believe that he exaggerates the exceptions which it suffers, and that it must be taken into account in the case of elements whose physical properties are very similar, as in the case of metals whose fusion points are not very far apart.

of the thermic properties of the reacting bodies. We may, by this new law, foresee the reciprocal actions of compounds towards one another and towards simple bodies, when we know the quantities of heat given out in the formation of each compound. This new law is no other than the third principle of the author, which has already been stated, the law of maximum work.

Whence the division of this volume in two parts :

The first treats of what may be called chemical dynamics. It is the study of combination and decomposition, and contains definitions of the opposing actions, on one side, of chemical forces, and on the other side, of calorific, luminous and electric energies, which determine the phenomena. In this way, the conditions are laid down which determine the existence and the stability of combinations for each separate body.

The second part is the study of the final state which results from reciprocal actions between simple and compound bodies ; this is chemical statics. In this part comes into action the principle of maximum work, which is as remarkable for its simplicity as for its generality. It brings everything down to the knowledge of two things : the heat given out by the transformations, and the stability which belongs to each compound.

The author demonstrates the existence of this principle, by the discussion of the general phenomena of chemistry ; afterwards, he develops the application of it to the reciprocal actions of the principal groups of substances, such, for instance, as take place between elements and binary compounds ; the reciprocal displacement of binary compounds, and specially of hydracids, when opposed to one another or to water ; the reciprocal displacements of acids in salts, and, finally, saline double decompositions.

It may be easily understood that it is impossible to give, in a review of this kind, a clear idea of a work of such importance and of such vast extent. We have only tried to give an idea of the subjects treated in it. The theories of M. Berthelot are well known, as they have been developed by him for the last sixteen years in a series of papers, which have been read by all chemists. Nevertheless, the present work forms an important epoch in the history of chemistry, and shows the necessity of transforming its methods. In the future, it will not be sufficient to state the reactions of which a body is susceptible, as if they were mere experimental data. It will be necessary to derive them from the general principles, of which these re-

actions are consequences. Doubtless, the edifice of chemical mechanics, whose foundations have been laid by M. Berthelot, cannot be considered as complete. Sixty years ago, the laws which govern chemical proportions were established, and nevertheless, the numbers which represent equivalents have frequently to be rectified. We may expect that those which express the quantities of heat of combination, or transformation, will also require change, more especially, as many of them cannot be determined directly by experiment, but result from complicated calculations in which a great number of reactions have to be taken into account.

There are, moreover, many theoretical questions of the highest importance, the solution of which is at present beyond our reach.

If the heat given out in the combination of two bodies, is the immediate consequence of the loss of momentum which comes from the union of their particles, and if it measures at the same time their mutual affinity, what then is the first cause of affinity? Is it a special force as was once believed? Or is it the concordance in the vibratory motions of the particles?

Those combinations which are attended with evolution of heat, are the only ones which can take place directly; but they do not always take place spontaneously. Many of them must be determined by an exterior cause, such as heat, light, electricity, but these agents do not give to the elements an energy of which they have already an excess. How then do they act?

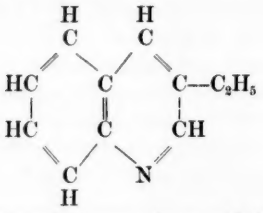
These questions, and many others which will come up, cannot fail to exercise for a long time to come the sagacity of chemists. At any rate, an important step has been made towards their solution when it it has been shown that the physical and chemical energies which come into play in chemical reactions, follow the laws of rational mechanics.

Abstracts from American and Foreign Journals.

Berichte der Deutschen Chemischen Gesellschaft.

Abstractor, H. ENDEMANN, Ph.D.

On the Synthesis of the Homologues of Hydrocarbostyrile and Chinolene, ADOLF BAEYER and O. R. JACKSON (**13**, 115).—Hydrocarbostyrile must be looked upon as the anhydride of ortho-amidohydrocinnamic acid, which as such, is not known, but which stands to the first in the same relation as orthocumaric acid to cumarine. Homologues of the orthocumaric acid were prepared by Perkin, by the action of salicylic aldehyde upon propionic, butyric and valerianic acids and sodium; and these, after nitration and reduction, should furnish homologues of hydrocarbostyrile. The latter are derived from the orthonitro acids merely, and if the crude product of nitration undergoes the process of reduction, amido acids are likewise formed from those nitro acids, wherein the nitro group is not in the ortho position. Thus the hydrocarbostyrile of phenylvalerianic acid was produced from phenylangelicic acid. This, by the action of phosphorus pentachloride, gives a body of the composition, $C_{11}H_{10}NCl$, which, with HI, gives a base, $C_{11}H_{11}N$, of the character of chinolene, and which must be looked upon as an ethylchinolene, the constitution of which is represented by the following graphic formula.



As regards further theoretical reasonings, and the description of the various reactions, mentioned above, the reader is referred to the original.

On Diphenyldiamidonaphthol, B. GOES (**13**, 123).—Martius' yellow, or dinitronaphthol potassium, under the influence of reducing agents forms diamidonaphthol. If its hydrochloric acid salt be heated with aniline to 100–130°, ammonia is developed and a diphenyl derivative is produced, which can easily be purified. Toluidine reacts in an analogous manner; the reaction, however, does not proceed with the same ease and regularity as the one mentioned above.

The Constitution of Nitrosodimethylmetatoluidine, C. RIEDEL (**13**, 126).

On the Action of Phosphonium Iodide, upon Bisulphide of Carbon, HANS. JAHN (**13**, 127).—The reaction is carried out in hermetically sealed tubes, at a temperature of from 120–140° C. The gaseous product of the reaction consists mainly of CH_4. A peculiar red crystalline substance, which contains phosphorus, carbon, sulphur, hydrogen and oxygen, in proportions corresponding nearest to the following formula, $C_9S_7P_6H_4O_{12}$, is likewise formed.

Some Derivatives of Ortho- and Paratoluidine, G. STAATS (**13**, 135).—This article contains the genesis and description of the following compounds:

Ortho- and paratolyl mustard oil.

Orthotolylsulpho-urea and paratolylsulpho-urea.

Orthotolylglycocol.

Aceto-orthohomoparoxybenzaldehyde.

On the Heat Evolved in the Formation of Cuprous Chloride, JULIUS THOMSEN (**13**, 138).—The author defends and furnishes further proof for his figure 59,625° C., against Berthelot's results, 54,200° C.

Niobite of the Iser Mountains, J. V. JANOVSKY (**13**, 139).—A niobite found by the author, associated with iserite and iserene, proved to be, on examination, a columbite, containing 16.25 per cent. of tantalic acid, and 62.64 per cent. of niobic acid. Iserite is represented by the formula, $FeTi_2O_5$. Iserene is a mixture, containing mainly titanates of iron, manganese and magnesia. Analyses of red and blue spinell and of zircon, from the same locality, are also given.

On a New Method to Determine the Specific Gravity of Liquids, H. SOMMERKORN (**13**, 143).—Will be noticed elsewhere.

Anethole Derivatives, F. LANDOLPH (**13**, 144).—The author describes the following derivatives of anethole or allyl-anisole; dihydro-anethole; tetrahydro-anethole; hexahydro-anethole; and some substances obtained by the action of potassium hydrate in alcoholic solution, upon anethole and monochlor-anethole.

Determination of Moisture in Air, F. RUEDORFF (**13**, 149).—Will be noticed elsewhere.

On the Heat Absorbed during the Formation of Cyanogen, JULIUS THOMSEN (**13**, 152).—The author calls attention to the fact, that he announced in 1854 (*Poggendorf's Annalen*, **92**, 55) that, in

the formation of cyanogen, a considerable quantity of heat is absorbed, which he calculates to 39,200° C., for the now accepted atomic weights. This is cited to meet a statement of Berthelot to the effect, that he had first called attention to this hitherto unknown fact, in 1864.

Contributions to the Knowledge of Pyridinetricarbonic Acid from the Alkaloids of the Quinine Group, S. HOOGEWERFF and W. A. VAN DORP (**13**, 152).—Skraup oxidized cinchoninic acid with potassium permanganate, and obtained a tricarbopyridinic acid, which he considered identical with the same obtained by the direct oxidation of the alkaloids of the quinine group, described by the authors. Experiments were made with the view to obtain further details, especially as regards the composition of the salts of the tricarbonic acid, whether obtained from quinine, or any of the other alkaloids of this group. They were invariably found to be identical, and, as far as could be ascertained, also identical with those obtained from Skraup's acid.

Determination of Oxygen Dissolved in Water, J. KOENIG (**13**, 154).—Will be noticed elsewhere.

Reactions in the presence of Aluminium Chloride and Bromide, G. GUSTAVEON (**13**, 157).—The author gives a short abstract of his discovery that aluminium chloride and bromide unite with unsaturated hydrocarbons; the products are either stable, and as such, easily prepared, or they may prove to be merely compounds which, under other influences, are easily transformed. This gives rise to what may be called the catalytic action of these aluminium compounds.

Preparation of Bioxyfumaric Acid, S. TANATAR (**13**, 159).

Maleic and Malic Acids from Alphabibrompropionic Acid, S. TANATAR (**13**, 159).

Etherification of the Non-saturated Monobasic Acids, N. MENSCHUTKIN (**13**, 162).—If acids and alcohols are allowed to react, ethers are formed up to a certain point, when the acid and alcohol remain uncombined. This limit for the reaction differs somewhat for various acids, but is generally found in the neighborhood of 70 per cent., 30 per cent. remaining uncombined.

The reaction, however, differs greatly, if we observe the initial velocity with which the reaction proceeds. It is greater for acids with low atomic weight; and in the case of acids with the same atomic weight, it is greatest with the primary, less with the secondary, and least with the tertiary acids.

This initial velocity, in a number of acids examined and given in this paper, was, for instance, in the neighborhood of 40 for primary, in the neighborhood of 12 for secondary, and 7 for tertiary acids. Thus we have a means of determining the structural formula of an acid by determining the initial velocity of etherification.

The Structural Formula of Sorbinic and Hydrosorbinic Acids, N. MENSCHUTKIN (**13**, 163).—The initial velocity of sorbinic acid was found to be 7.96 per cent.; it must, therefore, be looked upon as a tertiary acid—as propylmethylene carbonic acid. Sodium amalgam produces hydrosorbinic acid, which, having an initial velocity of 43.0 per cent., is a primary acid.

Belladonnine, K. KRAUT (**13**, 165).—The author found in commercial atropine, a base which he described in *Liebig's Annalen*, **148**, 236, and which he had called belladonnine. From later investigation he inclines to the belief, that belladonnine must be isomeric with atropine.

A New Chemical Photometer, JOSEF MARIA EDER (**13**, 166). —Will be noticed elsewhere.

On the Chemical Composition of Pyroxyline and the Formula of Cellulose, J. M. EDER (**13**, 169).—The author has come to the conclusion, that all pyroxylines must be looked upon as nitric ethers, for the following reasons :

1. Alkalies remove variable quantities of nitric acid, but also some nitrous acid, the formation of which is due to secondary reactions.

2. Pyroxyline, treated with oil of vitriol, forms a cellulose sulpho acid, losing all nitric acid.

3. Iron proto salts produce with it the same reactions as with other nitrates.

4. Pyroxyline, with sulphuric acid, over mercury, produces nitrogen oxide.

5. Reducing agents produce no amides, but simply reproduce cellulose.

The author produced the following compounds :

Cellulose hexanitrate,	$C_{12}H_{14}O_4(NO_3)_6$,	14.14 per cent.	N.
Cellulose pentanitrate,	$C_{12}H_{15}O_5(NO_3)_5$,	12.75 "	"
Cellulose tetranitrate,	$C_{12}H_{16}O_6(NO_3)_4$,	11.11 "	"
Cellulose trinitrate,	$C_{12}H_{17}O_7(NO_3)_3$,	9.15 "	"
Cellulose dinitrate,	$C_{12}H_{18}O_8(NO_3)_2$,	6.76 "	"

Cellulose hexanitrate is insoluble in a mixture of alcohol and ether, while the others are all soluble. The lower nitrates may be produced

from the higher nitrates, by treatment with a fixed alkali or ammonia. A cellulose mononitrate could not, however, be obtained. If the dinitrate be acted upon by alkalies, resinous substances and various organic acids are produced. Gun-cotton is, therefore, the hexanitrate, while for the production of collodion, the tetranitrate is employed.

On the Synthesis of Methylketole, an Isomere of Skatole, A. BAEYER and O. R. JACKSON (**13,** 187).

Contributions to the Knowledge of the Products formed by the Putrefaction of Albumen, E. SALKOWSKI and H. SALKOWSKI (**13,** 187).

Justus Liebig's Annalen der Chemie.

Abstractor, GEO. A. PROCHAZKA, Ph.D.

The boiling points of the Esters and Ether esters of the Oxi-acids, LUDWIG SCHREINER (**197,** 1–26).—The article refers to the preparation and regularities with regard to the boiling points (see also this JOURNAL, **1,** 290), of a series of esters and ether esters of glycolic, lactic, α-oxibutyric and salicylic acids.

The simple esters (oxi-acid compounds, with alkyl substituted in place of the hydrogen of the acid, OH) of glycolic, lactic and oxibutyric acid, are neutral colorless liquids, which are immediately decomposed by water. An increase of the alkyl by CH_2 is attended by a rise of the boiling point, by about 10°.

The esters of glycolic acid were obtained by the reaction of dry sodium glycolate, monochloracetic ester and the absolute alcohol in sealed tubes at 160°. $CH_2OH.COONa + CH_2Cl.COOC_2H_5 + C_2H_5OH = 2(CH_2OH.COOC_2H_5) + NaCl$.

Oxibutyric ethyl ester was obtained in like manner, in the reaction of sodium α-oxibutyrate, from butyric ethyl ester and alcohol, at 180°.

Lactic esters were obtained by heating pure lactic acid and absolute alcohol to 160°.

The glycolic ether esters are colorless neutral liquids, heavier than water, readily volatile with water vapor. They are very difficultly saponified. The compound lactic esters are partly insoluble in water. The α-oxibutyric ether esters are neutral liquids, of disagreeable odor, which are very sparingly soluble in water. The boiling points of the methyl esters are lower by about 19° than those of the corresponding oxi-acid ethers. An increase by CH_2 of the acid

alkyl in the ether esters, is attended by an increase of the boiling point, by about 6°; if the alcoholic alkyl is increased by CH_2, the boiling point rises by about 19°.

The glycolic ether esters were obtained by the gradual addition of monochloracetic esters to the diluted solutions of the sodium alcoholates, the lactic ether esters analogously in the reaction of sodium alcoholates and α-brompropionic esters, the α-oxibutyric ether esters in the reaction of sodium alcoholates and α–brombutyric esters (Duvillier).

The specific gravities of the esters and ether esters are decreased by the addition of the CH_2 group. The diminution is largest if the CH_2 group enters into the acid radical; smaller, if it enters into the alcoholic OH; still smaller when entering into the acid OH.

Salicylic esters were obtained by saturating alcoholic salicylic acid solution with HCl gas. Colorless liquids, which are insoluble in water and yield a violet coloration with ferric chloride. The compound ethers were obtained in the reaction of the esters, alcoholic potash and alkyl iodide. The yield was small, and the products could be obtained only in a state of approximate purity. Considerable difficulty was experienced in the preparation of ether esters containing two different alkyls, in consequence of a partial interchange of the alkyls in the course of the operation. An increase of the alkyl of the simple salicylic esters by CH_2, is attended by a rise of the boiling point by 6°. The boiling points of the compound esters rise by 2°, if the acid alkyl is increased by CH_2; by 21°, if the increase takes place in the alcoholic alkyl. The boiling point of the methylether of a salicylic ester is higher by 27°, than that of the corresponding simple ester.

Methyl- and Dimethyl-diacetonamine, TH. GOETSCHMANN (**197**, 27–47).—These bases correspond to the diacetonamine of Heintz, obtained in the reaction of ammonia upon acetone. Dimethyl-diacetonamine results in the reaction of dimethylamine upon acetone, most favorably at 100–105°. Platinum chloride produces in the mixture thus obtained a precipitate of a double salt of dimethylamine and dimethyl-diacetonamine, $(C_9H_{17}NO.C_2H_7N)H_2PtCl_6$, which is difficultly soluble in water, sparingly soluble in dilute alcohol, altogether insoluble in absolute alcohol and ether, and crystallizes in yellowish-red prisms. There is no method for the separation of the dimethyl-diacetonamine platinum salt in this salt. A separation of the bases was effected by converting the platinum salts into the gold salts. Dimethylamine gold chloride dissolves readily in water.

Dimethyl-diacetonamine gold chloride, $C_8H_{18}NOAuCl_4$, crystallizes in long, feathery needles, readily soluble in hot water, very difficultly in cold water and alcohol, insoluble in ether. *Dimethyl-diacetonamine hydrochloride* was prepared from the gold salt. It was obtained from the alcoholic solution in crystals, which are extremely deliquescent, and also extremely soluble in alcohol. The solutions of the salt undergo partial decomposition when heated on the water-bath; the decomposition is complete if the evaporation is carried to dryness.

The base could not be liberated by alkali, in consequence of decomposition; the products are dimethylamine and mesityloxide. *The platinum double salt*, $C_{16}H_{36}N_2O_2PtCl_6$, crystallizes in light red scales, which are insoluble in strong alcohol and ether. The *nitrate* and *sulphate*, obtained by double decomposition of the hydrochloride with the corresponding silver salts, crystallize with difficulty in small, extremely deliquescent needles. The acid oxalate crystallizes in deliquescent needles.

Methyl-diacetonamine was obtained by allowing the solution of methylamine in acetone to stand for several months. Alcoholic platinic chloride precipitates from the mixture the platinic and the platinous salts of the bases, which can be separated by the difference of their solubilities in water. $C_{14}H_{32}N_2O_2PtCl_6$ crystallizes in large, light red, rhombic prisms, which are tolerably soluble in water. $[(C_7H_{15}ON)HCl]_2PtCl_2$ crystallizes in dark red prisms. *Methyl-diacetonamine hydrochloride* is extremely deliquescent; the sulphate and nitrate were obtained in the form of colorless syrups. The *gold salt*, $C_7H_{15}NO.HCl.AuCl_3$, crystallizes in thin needles or short prisms, which are difficultly soluble in cold water, easily in hot water. The neutral oxalate is very deliquescent, but very difficultly soluble in absolute alcohol. The acid oxalate, which crystallizes in small, short prisms, is not deliquescent. The picrate crystallizes in yellow needles, which are only sparingly soluble in cold water, alcohol or ether, easily in hot water. Acetone bases, other than methyl-diacetonamine, also appear to form in the reaction of methylamine upon acetone.

Contribution to the Knowledge of Quinamine, A. C. OUDEMANS, JR. (**197**, 48–69).—The alkaloid *, discovered by Hesse as a constituent of the bark of *Cinchona succirubra*, was obtained from the crude mixture of bases, on removal of quinine and cinchonidine in the form of the neutral tartrates, by digesting the portion of the alkaloids soluble in ether, with boiling 50 per cent. alcohol. The

* Hesse, Ber. d. d. chem. Gesell., **5**, 265; **10**, 2157; Ann. Chem., **166**, 266; de Vrij, Pharm. J. and Trans. [3], **4**, 609; Howard, Pharm. J. and Trans. [3], **5**, 1.

boiling alcohol dissolves these alkaloids completely; on cooling, almost the entire quantity of quinamine separates. The same method was employed for the approximate quantitative determination of the base in the crude mixture of bases, which, in this manner, was found to contain about 4.5 per cent. of quinamine. The author's analyses of the alkaloid lead to the formula, $C_{20}H_{26}N_2O_3$, first assigned to it by Hesse; his iodine determinations, in the well crystallized iodohydrate, to Hesse's later formula, $C_{19}H_{24}N_2O_3$. 100 pts. of pure ether dissolve 2.06 pts. of the alkaloid (Hesse states that it is readily soluble). The following reactions are described as being very delicate for minute quantities of the alkaloid.

1. If a drop of quinamine salt solution is cautiously allowed to flow on concentrated sulphuric acid, containing a small quantity of nitric acid, the place of contact assumes a chestnut coloration in the case of more concentrated quinamine salt solutions, a beautiful orange coloration if the solution be less concentrated. The liquid, on subsequent gradual dilution with water, becomes at first purple, finally of a light rose color.

2. Characters written on paper, with a moderately concentrated solution of the alkaloid in a *slight* excess of sulphuric acid, become brown or olive colored, if placed over a mixture of a small quantity of potassium chlorate and concentrated sulphuric acid. If the paper is then removed, the characters gradually assume a rose color.

Quinamine salts. The author reaffirms the statements of Hesse, with regard to idohydrate, chlorohydrate, neutral and acid tartrate, neutral sulphate and acetate. Neither did he succeed in obtaining a crystallized bromohydrate, oxalate or acid sulphate. The *formate* was obtained in feathery crystals. The *nitrate*, $C_{19}H_{24}N_2O_2HNO_3$, crystallizes in monoclinic prisms; the *chlorate*, water-free, in forms of the rhombic system; the *perchlorate*, monoclinic; the *chloroplatinate*, $2(Ch.HCl),PtCl_4$, is difficultly soluble in pure water, easily in water that contains hydrochloric acid.

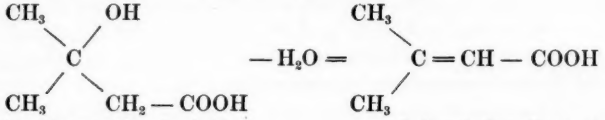
Quinamine is a monoacid base. With regard to the influence of quinamine upon the plane of polarization, reference must be had to the numerous details of the original.

Diallylisopropylcarbinol, C. RJABININ and ALEX. SAYTZEFF (**197**, 70–72).—Diallylisopropylcarbinol, $C_{10}H_{18}O$, which was obtained in the same manner as diallylpropylcarbinol,* is a colorless liquid, boiling point 182 to 185°, sp. gr. = 0.8647 (0°).

* Ann. Chem., **193**, 362.

On oxidation with chromic acid mixture, it yields carbonic and acetic acids.

Contributions to the History of the Oxivalerianic Acid, which forms on Oxidation of Allyldimethylcarbinol, ALEX. SEMLJANITZIN and ALEX. SAYTZEFF (**197**, 72–74).—By the reaction of PCl_3 upon the ethyl ether of oxivalerianic acid,* an acid was obtained in long glistening needles, m. pt., 68.5–69°, which the authors consider to be identical with the angelicic acid of Neubauer,† obtained on the oxidation of valerianic acid (from fermentation of amylic alcohol), and recently again examined by W. v. Miller.‡ The formation of the acid would be represented in



β-oxi-isopropylacetic Acid. *β*-dimethylacrylic Acid.

Behavior of some Nitro-compounds towards Hydrogen Sulphide, F. BEILSTEIN and A. KURBATORO (**197**, 75–85).

The authors find, as a general result of their investigation, that trisubstituted chlornitrobenzoles of unsymmetrical arrangement, are not reduced by H_2S. The Cl atom adjacent to a NO_2 group is exchanged for S or HS. If two NO_2 groups are next to each other, the nitro group nearest to the Cl enters into reaction with H_2S. Only in the case of not adjacent, or symmetrical, position, as in nitro–m–dichlorbenzole, H_2S effects a reduction of the NO_2 group.

1. *Chlor-m-dinitrobenzole,* $C_6H_3Cl(NO_2)_2$ (1.2.4), according to Jungfleisch,§ on reduction with Sn and HCl in aqueous solution, yields chloronitroaniline. The authors find this statement to be erroneous. The product obtained was chlor–m–phenylenediamine; m. pt., 86°; difficultly soluble in water, very easily in alcohol. Alcoholic ammonium sulphide, K_2S or KHS, convert the chlorodinitrobenzole into *m–dinitrophenylsulphide,* $[C_6H_3(NO_2)_2]_2S$. Yellow needles, difficultly soluble, or almost insoluble in the ordinary solvents, easily in concentrated nitric acid; m. pt., 193°. On treatment with the nitric acid (sp. gr. = 1.5) at 120°, the sulphide is coverted into *dinitrophenylsulphone,* $[C_6H_3(NO_2)_2]_2SO_2$, yellowish needles; m. pt., 240–241°.

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* Ann. Chem., **185**, 163.

† Ann. Chem., **106**, 65.

‡ Ber d. d. chem. Gesell., **11**, 1516.

§ Ann. Chim. Phys. [4], **15**, 231.

2. *Nitro-p-dichlorobenzole*, $C_6H_3ClNO_2Cl$ (1.2.4), on treatment with alcoholic K_2S, yields chloronitrophenylsulphide; with KHS (or NH_4HS) the mercaptan, $C_6H_3Cl(NO_2)HS$. *Chloronitrophenylsulphide* crystallizes in dark yellow needles, which are readily soluble in benzole, nearly insoluble in alcohol; m. pt., 149–150°. *Chloronitrophenylmercaptan*, yellow plates; m. pt., 212–213°. Alcoholic ammonium sulphide converts the mercaptan into a body, $C_{12}H_8Cl_2N_2S_3$ [or $\begin{matrix} C_6H_3ClSH.N \\ C_6H_3ClSH.N \end{matrix}\!\!>\!S(?)$], of basic properties, crystallizing in yellow needles, m. pt., 147°, which is readily oxidized when heated with nitric acid (1.34), yielding a substance, $C_6H_3ClN_2S$ (or $C_6H_3Cl\begin{matrix} N \\ S \end{matrix}\!\!>$), crystallizing in large colorless needles, m. pt., 103.5°, volatile with water vapor, which are readily soluble in the ordinary solvents.

3. *Chloro-o-dinitrobenzole* (1.3.4) yields *chlornitrophenylmercaptan* with alcoholic KHS. Yellow needles; m. pt. 171°.

4. *Symmetrical nitro-m-dichlorbenzole*, $C_6H_3Cl_2NO_2$ (1. 3. 5.), with alcoholic KHS, yields a precipitate of *tetrachlorazoxibenzide*, $(C_6H_3Cl_2)N_2O$, m. pt., 171–172°; the solution contains symmetrical m-dichloraniline.

Compounds of the Camphor Group, J. KACHLER, sixth paper, (**197**, 86–104).—*Borneo camphor.* The pure sublimed borneols obtained from two varieties of crude material were identical. Formula: $C_{10}H_{18}O$; m. pt., 197.5–198°; point of solidification, 195°; b. pt., 212°; rotation in acetic ether solution, α-D = + 32.7°. Nitric acid converts it into ordinary camphor. P_2Cl_5 at ordinary temperature, or fuming HCl, in sealed tubes at 100°, and borneol, yield borneol chloride, $C_{10}H_{17}Cl$, a white, camphory, optically active, substance, which is insoluble in water, easily soluble in alcohol or ether. M. pt., 157°. It undergoes decomposition easily. When heated with water to 90–95°, it yields borneo camphene, $C_{10}H_{16}$; m. pt., 51°; b. pt., 160–165°. On distillation alone, or with strong bases, borneol chloride yields liquid hydrocarbons principally. HBr and borneol appear to yield the bromide, $C_{10}H_{17}Br$; m. pt., 74–75°.

The artificial borneol obtained by the method of Baubigny,* appears from its general properties and behavior towards nitric acid and P_2Cl_5, to be identical with the natural. There is a difference in the

* Compt. Rend., **63**, 221.

optical behavior; the artificial product could, however, be separated into constituents of different optical behavior.

Glycyrrhizine, J. HABERMANN, first paper (**197**, 105–125).—The author finds that liquorice-root contains a peculiar nitrogenous tribasic acid, which forms neutral and acid salts. The acid potassium and acid ammonium salts crystallize, and are intensely sweet. The sweetness peculiar to liquorice-wood, is probably due to the presence of ammonium salts of glycyrrhizinic acid. The crystallization resulting from the solution obtained by digesting commercial *glycyrrhizine ammoniacale* with boiling glacial acetic acid, yields pure acid ammonium glycyrrhizinate on repeated recrystallizations, first from boiling glacial acetic acid, and then strong boiling alcohol. Acid ammonium glycyrrhizinate crystallizes in slightly yellowish, vividly glistening needles, which seem to correspond to the formula, $C_{44}H_{62}NO_{18}(NH_4)$. They are insoluble in ether, difficultly soluble even in boiling absolute alcohol, very soluble in boiling water. They become gelatinous in water of ordinary temperature. The solubility in water is very considerably increased by the addition of alkali. Neither the solution in water nor in dilute alcohol will yield the salt in crystals, but in the form of an amorphous brittle mass, having the appearance of albumen. The acid potassium glycyrrhizinate is a perfectly white, crystalline body, which exceeds in sweetness, levulose, cane sugar, or even the acid ammonium salt.

The neutral ammonium salt, $C_{44}H_{60}NO_{18}(NH_4)_3$, was obtained in the form of an amorphous, brittle, light brownish-yellow mass, which is extremely soluble in water and spirits, almost insoluble in absolute alcohol. The neutral potassium salt presented a yellowish-white loose friable mass, which is readily soluble in water. The barium salt was obtained by the addition of baryta water to the hot solution of the acid ammonium salt in spirits, as a yellowish flocculent precipitate, which is sparingly soluble in water. The *lead* salt is amorphous, brittle, soluble in glacial acetic acid, sparingly soluble in water, insoluble in alcohol or ether. Glycyrrhizinic acid, $C_{44}H_{69}NO_{18}$, obtained by decomposition of the lead salt by H_2S, has the appearance of dried egg albumen. It becomes gelatinous in cold water, yields a clear sticky solution in boiling water, is pretty soluble in spirits and boiling glacial acetic acid, sparingly in absolute alcohol or ether. It becomes brown at 100°; the taste is sweet; the acid decomposes the carbonates of the alkaline earths gradually on boiling. It reduces Fehling's solution on heating, nearly as rapidly as grape sugar.

Hydrogen Peroxide, sixth paper, EM. SCHOENE (**197**, 137–168). *Behavior of hydrogen peroxide towards the galvanic current.*—The very elaborate and careful experiments lead to the conclusion that hydrogen peroxide is not an electrolyte. In the course of the action of the galvanic current upon aqueous (acidulated) solutions of hydrogen peroxide, the solvent water (acid) alone is subjected to electrolysis, the decomposition of the hydrogen peroxide in the electrolytical liquid is a secondary reaction, consequent upon the reducing action of the electrolytical decomposition products of water, in nascent condition, upon the H_2O_2 around the electrodes:

(1) $O + H_2O_2 = H_2O + O_2$ (2) $H_2 + H_2O_2 = 2H_2O$; or rather
(1) $SO_4 + H_2O_2 = H_2SO_4 + O_2$ (2) $H_2 + H_2O_2 = 2H_2O$.

From this, it follows that hydrogen peroxide cannot form in the electrolysis of water.

The two Isomeric Bromides, $C_3H_6Br_2$, E. ERLENMEYER (**197**, 169–185).—A critical examination of the methods for the preparation of trimethylene bromide, from allyl bromide and HBr, of Kaysser,* Lermontoff,† Reboul‡ and Bogomoley,§ leads to the following results:

1. The most favorable conditions for the formation of trimethylene bromide are, (*a*) the maintenance of the largest possible excess of dry HBr to dry allyl bromide, to the conclusion or interruption of the reaction; (*b*) a temperature of 30–40°.

2. The more dilute (either by water or trimethylene bromide already formed) the HBr acts upon allyl bromide, the more considerable the formation of propylene bromide, in the course of the reaction, will be. After a certain degree of dilution has been attained by the formation of trimethylene bromide, the total residual HBr combines with allyl bromide very slowly at low temperature, pretty rapidly at high temperature, yielding only propylene bromide.

3. In sufficiently concentrated HBr solutions, even at temp. 0–30° or above 100°, the reaction always begins with the formation of trimethylene bromide; the formation of propylene bromide seems to begin in less dilute HBr solutions at low temperatures than at high temperatures.

The author has modified the original method of Kaysser in conformity with these results.

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* Inaug. Diss. Muenchen, 1875.
† Ann. Chem., **182**, 358.
‡ Ann. Chem. Phys. [5], **14**, 470.
§ Ber. d. d. chem. Gesell., **11**, 1257.

Oxichloride and Chlorides of Tungsten, HUGO SCHIFF (**197,** 185, 193).—The author has repeated his experiments with regard to the action of P_2Cl_5 upon WO_3 (Ann. Chem., **102,** 111). He reaffirms his previous results. Oxichlorides, tungsten oxitetrachloride ($WOCl_4$) principally, are formed at first, these, by the further action of P_2Cl_5 at *higher* temperature and pressure, yield hexachloride, which latter compound is partially decomposed to pentachloride and chlorine. (Compare Teclu, Ann. Chem., **187,** 255).

Influence of the Isomerism of the Alcohols and Acids in the Formation of Compound Ethers, N. MENSCHUTKIN, second paper (**197,** 193, 225).—*Formation of the acetic ethers of the secondary alcohols.* Results similar to those in the case of primary alcohols* were obtained.

		Initial Velocity.		Limits.
		absolute.	relative.	
a.	1. Dimethylcarbinol,	26.53	43.85	60.52
	2. Ethylmethylcarbinol,	22.59	38.10	59.28
	3. Hexylmethylcarbinol,	21.19	34.16	62.03
	4. Isopropylmethylcarbinol,	18.95	31.95	59.31
	5. Diethylcarbinol,	16.93	28.86	58.66
b.	6. Ethylvinylcarbinol,	14.85	28.42	52.25
	7. Diallylcarbinol,	10.60	21.14	50.12

a. Saturated secondary alcohols. *b.* Secondary non-saturated alcohols. Experiments performed at 154° (see this JOURNAL, **I,** 256).

The absolute initial velocity of the first member of the series is greatest; the initial velocities of the saturated secondary alcohols of equal structure (2 and 3) appear to be constant; of the saturated secondary alcohols of different structure (4 and 5), they are lowest. The absolute initial velocity of non-saturated secondary alcohols decreases with their distance from the saturated series. In the further course of etherification the velocities of the secondary alcohols are greater than those of the primary alcohols. The relative initial velocities decrease with the increase of the molecular weight. The absolute and relative velocities, and limits of etherification, of the secondary alcohols, are considerably lower than of the primary alcohols, a *characteristic distinction* between the two series of alcohols.

Formation of the acetic ethers of the tertiary alcohols. Saturated tertiary alcohols. The process of etherification is more complicated than in the case of primary and secondary alcohols. It is normal during the first hours only. In the further stages, the reaction products are ether, water, alcohol, acid, and *olefines.* The process of etherification combines the following reactions: 1. Formation of

* See this JOURNAL, **I,** 256.

ether and water; 2. Decomposition of ether by the water formed; 3. Dissociation of the ether to olefine and acid, and possibly; 4 and 5. Combination of the alcohol with water and acid, to alcohol and ether. The formation of olefine disturbs the ratio of equal molecules of acid to equal molecules of alcohol; the limits actually found are lower than the true limits, and hence not comparable with those of the primary and secondary alcohols. In the case of acetic etherification of trimethylcarbinol, at 154°, the relation, after the limit has been reached, may be expressed in the equation:

$$11C_2H_4O_2+11C_4H_{10}O=10C_2H_4O_2+C_2H_3(C_4H_9)+6C_4H_8+4C_4H_{10}O+7H_2O$$

The formation of isobutylene is less considerable at 100°, corresponding to a higher limit, represented in $16C_2H_4O_2 + 16C_4H_{10}O = 14C_2H_4O_2 + 2C_2H_3(C_4H_9)O_2 + 3C_4H_8 + 11C_4H_{10}O + 5H_2O$.

The absolute initial velocities only, are comparable with those of the primary and secondary alcohols, and are very low.

	Abs. In. Vel.	Limits. at 154°
Trymethylcarbinol	1.43	6.59
Ethyldimethylcarbinol	0.87	2.53
Diethylmethylcarbinol	1.04	3.78
Propyldimethylcarbinol	2.15	0.83
Isopropyldimethylcarbinol	0.86	0.85

The limits are reached in a short time, generally after twenty-four hours.

The behavior of the *non-saturated tertiary alcohols*, is similar to that of the saturated. The relation of the limits of the tertiary alcohols appear from the following tabulation.

$C_nH_{2n+2}O$		$C_nH_{2n}O$	$C_nH_{2n-2}O$
Diethylmethylcarbinol,	3.78	Allyldimethyl-carbinol,	
Isopropyldimethylcarbinol, $C_6H_{14}O$	0.83	($C_6H_{12}O$), 7.26	.....
Propyldimethylcarbinol,	0.85		
.....		Allyldiethyl-carbinol,	Diallylmethyl-carbinol,
		($C_8H_{16}O$), 4.72	($C_8H_{14}O$), 5.36
.....		Allydipropyl-carbinol,	Diallylpropyl-carbinol,
		($C_{10}H_{20}O$), 0.46	($C_{10}H_{18}O$), 3.10

The introduction of more complicated groups decreases the limits. The limits of the saturated alcohols are smaller than those of the non-saturated, etc. The stability of the ethers increases with the distance from the saturated series. Allydimethylcarbinol only is etherified in the first hour. (Initial velocity, 3.05 per cent.)

The behavior of the *phenols* on *acetic etherification* demonstrate that they are non-saturated tertiary alcohols. The course of etherification is normal.

	Initial Velocity.	Limit.
Phenol, C_6H_6O	1.45	8.64
Paracresol, C_7H_8O	1.40	9.56
Thymol, $C_{10}H_{14}O$	0.55	9.46
Naphthol, $C_{10}H_8O$	——	6.16

Contributions to the Knowledge of Cinchonidine, ZD. H. SKRAUP and G. VORTMANN (**197**, 226–243).—The authors have subjected the carefully purified base and a series of its salts, to renewed examination, which leads to the conclusion that the formula is not $C_{20}H_{24}N_2O$, as usually assumed, but $C_{19}H_{22}N_2O$. Platinum salt, $C_{19}H_{22}N_2O(HCl)_2PtCl_4 + H_2O$; the water escapes completely at 130°. Chlorohydrate, $C_{19}H_{22}N_2O.HCl + H_2O$. The neutral sulphate of the pure base shows all those properties which Hesse describes as being distinctive for homocinchonidine. It loses its water of crystallization very easily at ordinary temperature, and takes it up again, in part, in moist air. These facts lead to the supposition that homocinchonidine is nothing else than pure cinchonidine. Cinchonidine melts at 210.5°, without decomposition. Point of solidification, between 188° and 197°.

On oxidation with $KMnO_4$, at ordinary temperature, cinchonidine yields formic acid and cinchotenidine, which is isomeric with the cinchotenine obtained from cinchonine under like conditions. $C_{19}H_{22}N_2O + 4O = C_{18}H_{20}N_2O_3 + CH_2O_2$. Cinchotenidine, $C_{18}H_{20}N_2O_3 + 3H_2O$, crystallizes in colorless needles, which are difficultly soluble in absolute alcohol and cold water, more readily in the hot solvents, easily in dilute acids or alkalies. The aqueous solution reacts neutral. CO_2 precipitates it from the alkaline solution. The behavior towards Ag, Cu and Pb salts, is perfectly analogous to that of cinchotenine; m. pt., 256°. The chemical character of the body appears to be that of a phenol. The potassium compound and chlorohydrate were obtained as syrups. The *neutral sulphate*, $(C_{18}H_{20}N_2O_3)_2H_2SO_4 + 2\frac{1}{2}H_2O$, crystallizes in small white prisms, which are extremely soluble in water. Platinum double salt, $(C_{18}H_{20}N_2O_3)_2(HCl)_4PtCl_4$, was obtained from the hot dilute hydrochloric acid solution in large colorless plates.

Composition of Cinchonine, ZD. H. SKRAUP (**197**, 352–374).—The author's analyses of the carefully purified base and a series of its salts, proved it to correspond to the formula, $C_{19}H_{22}N_2O$, not to $C_{20}H_{24}N_2O$, generally assigned it. The pure alkaloid melts at 268.8°; the point of solidification was found between the limits 209° and 250°.

Platinum salt, $C_{19}H_{22}N_2O(HCl)_2PtCl_4$, light yellow precipitate, which becomes crystalline on standing. The neutral sulphate, $(C_{19}H_{22}N_2O)_2\,H_2SO_4 + 2H_2O$, of the *pure* base, crystallizes in thick prisms. Other forms were observed *only* when the base was not entirely pure. M. pt., 196°. The pure dehydrated salt is very hygroscopic. Thick masses of the salt, after protracted drying, melt at 115° and 130°, being converted into cinchonidine sulphate, without loss of weight. The chlorohydrate, with 2 mols. water, crystallizes in white, long thin prisms. Neutral iodide, with 1 mol. H_2O, in very slightly yellowish, small needles; loses its water at 100°.

The cinchonine in commercial cinchonine, is accompanied by another alkaloid, from which it is very difficult to separate, distinguished by its great resistance towards $KMnO_4$. This base has been designated by the author as cinchotine, and is identical with the hydrocinchonine of Caventou and Willm. Cinchotine corresponds to the formula, $C_{19}H_{24}N_2O$. The sulphate, $(C_{19}H_{24}N_2O_2)H_2SO_4 + 12H_2O$ (?) crystallizes in thin brittle prisms. The dehydrated salt is very brittle; it gradually takes up 2 mols. H_2O. The platinum double salt, $C_{19}H_{24}N_2O(HCl)_2PtCl_4$, was obtained from the hot dilute HCl solution, in orange colored granular crystals.

Oxidation Products of Cinchonine, Zd. H. Skraup (**197**, 374–384).—Potassium permanganate acts upon cinchonine sulphate at ordinary temperature, yielding cinchotenine, $C_{18}H_{20}N_2O_3$, and formic acid, $C_{19}H_{22}N_2O + O_4 = C_{18}H_{20}N_2O_3 + CH_2O_2$. Cinchotenine crystallizes in white needles, which melt at 197–198°, under partial decomposition. It is pretty soluble both in hot and cold water, very difficultly in absolute alcohol. It contains water of crystallization. The platinum salt, $C_{18}H_{20}N_2O_3 2HCl + PtCl_4$, crystallizes in large orange prisms.

Action of Oxidizing Agents upon the Hydrocarbons of the C_nH_{2n} ***Series,*** O. and F. Zeidler (**197**, 243–256).—The authors have allowed potassium permanganate, in neutral, acid and alkaline solutions, chromic acid, mixtures of potassium bichromate and sulphuric acid, to act upon ethylene, propylene, isobutylene and amylene, at ordinary temperature and at 100°. The action of permanganate, giving the larger yield of bibasic acids, was found to be more energetic than of chromic acid. Chromic acid yields monobasic acids (formic, acetic, etc.) principally, bibasic acids (oxalic, succinic, etc.) only in small quantities. In both cases, however, the same acids are formed. In all cases under examination, it was found that the oxidizing agents attack the olefines at the double linking of the carbon atoms.

Nitro-, Amido- and Bromsulphobenzol Acids, L. SPIEGELBERG (**197**, 257–306).—The very lengthy memoir gives in detail the modes of preparation, properties and analyses, of the following bodies:

Amidobromsulphobenzol acid, $C_6H_3.\overset{1}{S}O_3H.\overset{3}{N}H_2.\overset{4}{B}r$, and its potassium, barium, calcium, lead and silver salts.

Dibromsulphobenzol acid, $C_6H_3.SO_3H.Br_2$ (1.3.4), and its barium and lead salts. Dibromsulphobenzol acid (1.2.4) and its barium salts. The dibromsulphobenzol chlorides and amides, obtained from these acids.

Amidodibromsulphobenzol acid, $C_6H_2.SO_3H.NH_2.Br.Br$ (1.3.4.6), and the potassium, barium and lead salts.

Tribromsulphobenzol acid (1.3.4.6), and the barium and potassium salt. Tribromsulphobenzol chloride, tribromsulphobenzol amide.

Amidotribromsulphobenzol acid, $C_6H.SO_3H.Br.NH_2.Br_2$ (1.2.3.4.6), and its ammonium, potassium, barium and lead salts. Nitrodibromsulphobenzol acid; amidodibromsulphobenzol acid, $C_6H_2.SO_3H.Br_2.NH_2$, (1.3.4.6), and its ammonium, potassium, barium, calcium, lead and silver salts.

Nitrotribromsulphobenzol acid, $C_6H.SO_3H.Br_2.NO_2.Br$ (1.3.4.5.6), the ammonium, potassium, barium, calcium, lead and silver salts. The corresponding amido acid and salts of the amido acid. The diazo-compound, $C_6H\begin{cases}Br_3\\N=N,\\SO_3\end{cases}$ obtained from this acid.

Tetrabromsulphobenzol acid (1.3.4.5.6), the ammonium, potassium, barium, calcium, lead and silver salts. Tetrabromsulphobenzol chloride, tetrabromsulphobenzol amide.

Nitrotetrabromsulphobenzol acid, $C.SO_3H.No_2.Br_4$ (2.3.4.5.6), and ammonium, potassium, barium, calcium and lead salts. Nitrotetrabromsulphobenzol chloride, nitrotetrabromsulphobenzol amide. Amidotetrabromsulphobenzol acid, its potassium, barium and calcium salts. The diazo-compound, $C_6\begin{cases}Br_4\\N=N.\\SO_3\end{cases}$

Pentabromsulphobenzol Acid, HEINZELMAN and SPIEGELBERG, (**197**, 306–320).—The following results were obtained:

1. Pure pentabromsulphobenzol acid can be easily prepared from the amidotetrabromsulphobenzol acid, $C.\overset{1}{S}O_3H.\overset{2}{N}H_2.Br_4$. The acid is very readily soluble in water, the salts are extremely sparingly soluble. The chloride melts at 153-154°. 2. The amido acid, $C.\overset{1}{S}O_3H.\overset{2}{B}r.\overset{3}{N}H_2.Br_3$, is easily reduced to acids containing less bromine. It yields the

same pentabrom-acid, contaminated, however, with the tetrabrom-acid. 3. The pentabrom acid of Beckurts * and Langfurth,† contained tetrabrom acid, which is indicated by the lower m. pt. of the chloride, and greater solubility of the salts prepared by them.

Action of Dehydrating Bodies upon Camphoric Acid and its Amides, M. BALLO (**197**, 321–341).—Camphoric acid, on distillation with fused zinc chloride or phosphoric acid, is decomposed, principally according to the equation:

$$C_8H_{14}(CO_2H)_2 = C_8H_{14} + H_2O + CO_2 + CO.$$

C_8H_{14} = campholene, a colorless liquid, which is identical with Gille's ‡ campholene. A portion of the acid is carbonized, undergoing a more complicated decomposition, in which it yields *camphoterpene*, $C_{20}H_{32}$ (b. pt., 160–280°). It was found that the amides could not be obtained in the presence of water. A solution of camphoric anhydride in absolute alchohol was saturated with dry ammonia. Crystals of ammonium camphoraminate were obtained, and a mother liquid which, on evaporation, leaves a syrup. This syrup appears to contain an amide or the above ammonium salt, as it yields camphoricimide, $C_{10}H_{14}O_2NH$ (Laurent), and ammonia, on distillation. The camphoraminate, on distillation with ZnCl, yields the same products as camphoric acid.

$$C_8H_{14}(CONH_2CO_2NH_4)_2 + ZnCl + 2H_2O = 2NH_4Cl + C_8H_{14}\begin{matrix}CO.O\\CO.O\end{matrix}\!\!>\!\!Zn.$$

$$C_8H_{14}C_2O_4Zn = C_8H_{14} + CO + CO_2 + ZnO.$$

Anhydrous phosphoric acid also saponifies the larger part of the ammonium camphoraminate, yielding the above mentioned products. A portion of the salt is, however, converted into the *nitrile*, $C_{10}H_{14}N_2$, a colorless, crystalline body, which is isomeric with nicotine.

The chloride, $C_{10}H_{16}Cl_2$, of Pfaundler,§ is oxidized to complicated chlorine compounds in the first stages of the action of nitric acid upon it, camphoric acid being the final product.

The author regards camphor as the tertiary alcohol of

$$(C_9H_{15})'\cdot'''H - C - \overset{IV}{C} - OH$$
$$\qquad\qquad\quad \|$$
$$\qquad\qquad\quad C_8H_{14}$$

which would make borneol the secondary, menthol the primary

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* Ann. Chem., **181**, 226.

† Ibid, **191**, 205.

‡ Inaug. Diss., Goettingen, 1872.

§ Ann. Chem., **115**, 29.

alcohol; campholene, from the fact of the formation of crymol from camphor, may be regarded as $CH_3 - C = C - C_3H_7$ with CH_2—CH_2 bridging the two carbons.

Contribution to the Knowledge of Amidines and Thiamides of Monobasic Organic Acids, A. BERNTHSEN (**197**, 341–351).—*Ethers of imidothionic acids.*—Phenylacetothiamide and ethyl iodide combine below 100°. From the freshly prepared solution of this body NaOH precipitates *phenylacetimidothiethyl ether*,

$$C_6H_5 - CH_2 - C\begin{matrix}\diagup\!\!\diagup NH \\ \diagdown SC_2H_5\end{matrix}$$

an oily body, corresponding in its properties to those previously described by the author.*

When carefully heated, it is decomposed according to the equation:

$$C_{10}H_{13}NS = C_6H_5.CH_2.CN - C_2H_5HS.$$

The same base was obtained by the method of Pinner and Klein,† by conducting HCl into a mixture of benzylcyamide and mercaptan.

Benzimidothiethyl ether, $C_6H_5 - C\begin{matrix}\diagup\!\!\diagup NH \\ \diagdown SC_2H_5\end{matrix}$ was obtained in the manner indicated, from benzothiamide and C_2H_5, and in the reaction of $HCl.C_6H_5CN$ and C_2H_5SH.

Benzimidothiobenzyl ether, $C_6H_5 - C\begin{matrix}\diagup\!\!\diagup NH \\ \diagdown SC_7H_7\end{matrix}$ was obtained as well in the reaction of benzothiamide and benzyl chloride, as in the reaction of benzonitrile, benzylsulphydrate and HCl. From this it would follow that the amidothio-ethers of Pinner and Klein ‡ and the compounds of Wallach, belong to the same class of substances.

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* Ann. Chem., **192**, 57.

† Ber. d. d. chem. Gesell., **11**, 1825.

‡ Ber. d. d. chem. Gesell., **11**, 1509.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office,** by ARNO BEHR.

February 6th, 1880.

226,151.—*Distillation of oils.* WILLIAM ATWOOD.

The patent is for a special construction of the distilling apparatus.

226,153.—*Petroleum distillate for lubricating purposes.* WILLIAM ATWOOD.

Claims a fraction of the oil having a specific gravity of 20–16° Bé, and possessing lubricating qualities.

226,187.—*Apparatus for testing oil by electricity.* FRANCIS S. PEASE.

226,259.—*Vulcanisation of water-proof fabrics.* WILLIAM ABBOTT.

Claims the vulcanisation of fabrics containing an external or an intermediate layer of india-rubber, by submitting them to the action of chloride of sulphur.

Re-issue 9,144.—*Dye-stuff or coloring matter.* HEINRICH CARO.

Re-issue of patent 204,799.—*For "fast red."*

Consisting of the product made from diazonaphthalene-sulpho acid and beta-naphthol.

April 13th, 1880.

226,397.—*Process and apparatus for manufacturing gas.* MAHLON S. FROST.

A heating gas is produced first, by partial combustion in a generation of some carbonaceous material. This gas is mixed with air and passed through a second bed of coal, in a second generator, heating this coal to incandescence during its passage. When the coal is sufficiently hot, steam is passed through it, and water gas generated. This is finally carburetted in the first generator, for use as an illuminating gas.

226,398.—*Process of manufacturing glucose.* . CLINTON FURBISH.

Claims the separation of the hull and germ from the starchy portion of the corn, and the treatment of this starchy portion, with water and steam under pressure, preparatory to its conversion into glucose.

226,400.—*Manufacture of iron.* ROBERT H. HAMILTON and WILLIAM GRIFFITH.

Into the molten metal is mixed a certain proportion of muriate of ammonia, or a mixture of muriate of ammonia, black oxide of manganese, sal-soda, common salt and nitrate of sodium.

226,434—*Process of manufacturing glucose.* JOHN F. WOLFF.

The inventor proposes to force currents of air through the liquid during the ordinary process of the conversion of starch into glucose, by means of sulphuric acid, and claims to obtain a larger yield and a lighter color of the product.

226,447.—*Softening, plumping and depilating hides and skins.* JAMES FOLEY.

A solution of barium sulphide is employed.

226,467.—*Preservation of butter.* THOMAS F. WILKINS.

Uses metaphosphoric acid mixed with the butter.

226,506.—*Process of extracting the fibres from textile plants.* PAUL A. and M. A. FAVIER.

This process seems to consist essentially in a treatment of the plants, with steam under pressure.

226,547.—*Composition of matter.* JOHN L. POPE.

A mass consisting of pulverized cork, mixed with a suitable binder and with any substance susceptible to take a polish, the whole solidified by pressure.

226,572.—*Manufacture of hard rubber or vulcanite.* HEINRICH OTTO and MAX TRAUN.

Claim : the use of glass in the manufacture of vulcanite.

April 20, 1880.

226,583.—*Plastic composition of matter for the manufacture of jewelry and fancy articles.* ISAAC B. ABRAHAMS.

A compound consisting of glue, rosin and starch.

226,616.—*Anode.* JACOB KLEINHANS.

Makes nickel anodes with hook-shaped ends, whereby two or more may be readily united or detached.

226,632.—*Manufacture of nitrogen gas.* THOMAS B. STILLMAN.

Nitrogen gas is deprived of the last traces of oxygen by passing it over melted sodium, after it has been thoroughly dried by phosphoric anyhdride or some other strong absorbent for water.

226,738.—*Composition for filling teeth.* THOMAS FLETCHER.

Consists of a solution of phosphate of tin in phosphoric acid, combined with lime, silica and alumina fused together, and reduced to powder.

226,758.—*Composition for white-wash.* ARCHIBALD H. KERR.

Lime, whiting, plaster of paris, glue, carbonate of soda, borax and sulphate of soda.

226,839.—*Apparatus for testing lubricating oils.* CHARLES N. WAITE.

April 27, 1880.

226,844.—*Substitute for hard rubber.* GUSTAVUS A. FUDICKAR.

Ebony wood saturated with oil at a gradually augmenting temperature, so as to render it flexible.

226,867.—*Process of manufacturing nitro-glycerine.* FREDERICK MANN.

Nitro-glycerine is separated from its acid mother liquid, often cooling the mixture, and causing the nitro-glycerine to crystallize.

226,920.—*Compound soap.* EDWARD LYON.

Water, sixty gallons; Babbitt's best soap, twenty cakes; aqua ammoniae fortior, half a pint; sal-soda, ten pounds; salt, one gill; hyposulphite of soda, one pound.

226,933.—*Preparation for coating ingot moulds.* AUGUSTUS L. SIMONDI.

100 parts of tallow and 27 of lamp black.

226,965.—*Extracting gold, etc., from ores.* JOHN F. BOYNTON.

Consists in the treatment of the ore with chlorine gas, in an apparatus constructed for that purpose.

227,018.—*Process and apparatus for distilling alcohol.* GEORGE W. KIDD.

Distillation under a partial vacuum and at a low temperature.

227,027.—*Apparatus for the manufacture of nitric acid.* PAUL MARCELIN.

Brief: May use stem-valves in place of hand-holes.

227,032.—*Manufacture of bicarbonate of soda.* WILLIAM T. MENZIES.

In a solution of commercial carbonate of soda, the caustic soda is neutralized by carbonic acid, then the sulphur compounds are oxidized with chloride of lime, and, finally, bicarbonate of soda is precipitated from the clear solution by carbonic acid.

227,076.—*Galvanic Battery.* FERDINANDO TOMMASI.

227,080.—*Roofing and paving material.* CYRUS M. WARREN.

Coal-tar residuum is fused with wax tailings, candle-tar, fat or fat-oil, and a compound of natural bitumen, or asphaltum, with petroleum residuum.

Foreign Patents.

Condensed from R. BIEDERMANN'S Report to the German Chemical Society,

by OTTO H. KRAUSE.

O. BRAUN, Berlin: *Apparatus for cooling and warming gases mixed with vapors of liquids.* (Germ. P., No. 8585, July 19, 1879.)—A square tank with suitable openings for the admission of the vapors, &c., and for the exit of the condensed liquid and uncondensed gases. A second vessel, from the bottom of which wide cooling pipes, closed at their lower ends, project into the tank, forms the cover. A third vessel, with open tubes passing into and nearly reaching the bottom of the cooling pipes, is placed above it. The cooling liquid flows from the third vessel down through the tubes into the cooling pipes, and rises up in them into the second vessel, whence it is drawn off.

KARL MOELLER, Kupferhammer, near Brackwede: *Apparatus for filtering gases and vapors.* (Germ. P., No. 8806, June 17, 1879.)—The apparatus contains several independent, vertical, horizontal or inclined chambers. The gases to be filtered are made to pass through fine sieves, or through filters of cotton, mineral wool, or asbestos, which retain the suspended particles of liquid or dust.

ALEXANDER MUELLER, Berlin: *Preparation of a metallic plush for use in filtering under pressure.* (Germ. P., No. 9248, July 22, 1879.)—A perforated plate, the holes of which are filled with parallel wires, the ends projecting on the pressure side, and held in place by adjustable wedges. It is advantageous to apply a layer of asbestos to the back of the plate.

A. MARIA Y GARCIA, Aquilas: *Desilverisation of lead.* (Engl. P., No. 708, February 21, 1879.)—Antimony and iron are removed by blowing air through the molten metal. The resulting scum contains besides plumbic oxide, antimonic and ferric oxides. After removing it, the lead is desilverized with the aid of zinc. The oxides are treated with pyroligneous acid, and the solution, separated from the antimonic oxide, worked up into acetate of lead. The oxides, rich in silver, are also treated with acetic acid, and cupellation thereby avoided.

J. F. N. MACAY, Charapots, Ecuador: *Method for preparing ferric oxide and cupric chloride simultaneously.* (Germ. P., No. 9565, November 20, 1879.)—A solution of ferric chloride and cupric oxichloride are heated to boiling in the presence of air. For the ferric chloride, ferric sulphate and sodium chloride may be substituted.

K. and T. MOELLER, Kupferhammer, near Brackwede: *Purification of waste waters containing suspended matters.* (Germ. P., No. 9276, October 11, 1879; addition to Germ. P., No. 7014, August 20, 1878.)—Instead of passing carbonic acid into the waste waters treated with lime, as formerly proposed, they are made to pass through a graduation house, or over a slightly inclined plane, the carbonic acid in the atmosphere precipitating the lime.

ACTIENGESELLSCHAFT CROIX, at Croix: *Improvements in the manufacture of alkaline carbonates by means of trimethylamine.* (Germ. P., No. 9376, September 9, 1879; addition to Germ. P., No. 5786, October 6, 1878.)—Claims the application of mono- and dimethylamine, mono-propylamine and mono-isobutylamine, contained in commercial trimethylamine.

FELIX DE LALANDE, Paris: *Method of preparing green coloring matters by treating the sulpho derivatives of dibenzylaniline, dibenzyltoluidine and dibenzyldiphenylamine, with oxidizing agents.* (Germ. P., No. 9569, July 25, 1879.)—According to the strength of the sulphuric acid employed to react upon the above mentioned bodies, insoluble or soluble sulpho derivatives may be obtained. The former, for instance, by heating 10 pts. dibenzylaniline with 30–40 pts. sulphuric acid, of sp. gr. 1.834, to 150–170° C.; the latter, by digesting with four times its weight of fuming sulphuric acid, at 160° C. The sulpho acids are dissolved in calcium or sodium hydrate, and oxidized with potassium bichromate and acetic acid. The coloring matter is precipitated by excess of sodium chloride, mixed with 2–3 parts of sodium acetate, and dried. The liquid which contains the soluble sulpho acids is neutralized, and sulphates and coloring matter precipitated by barium chloride. Boiling solution of sodium hydrate extracts the coloring matter from the precipitate. The coloring matters are acids soluble in water, forming alkaline salts which are but slightly colored. The goods are first passed through an alkaline bath and finished in an acid solution.

C. N. HAKE, Douglashall, Westeregeln: *Manufacture of potassium sulphate from carnallite salts.* (Germ. P., No. 9108, October 13, 1878.)—Crude Stassfurt salts (containing about 16 per cent. of potassium chloride, as carnallite), are dis-

solved in the least amount of water, and the solution mixed with gypsum and kieserite. The following reaction takes place:

$$4(KCl + MgCl_2) + MgSO_4 + CaSO_4 =$$
$$(K_2SO_4 + CaSO_4) + 2(KCl + MgCl_2) + 3MgCl_2.$$

Potassium sulphate is extracted by boiling water from the calcined double sulphate of potassium and calcium.

JOSEPH TOWNSEND, Glasgow: *Manufacture of soda, potash, sulphuric acid and chlorine.* (Engl. P., No. 1703, April 30, 1879.)—This invention relates to processes in which magnesium and aluminium salts and silicic acid come into use. Most of the reactions have long been known.

1. 50 kgm magnesium sulphate and $48\frac{3}{4}$ kgm sodium chloride are intimately mixed and heated in a retort, to 210° C., steam being admitted. Hydrochloric acid is evolved, sodium sulphate and magnesia remain. (This process was worked by Raman de Luna, in 1855.)

2. 50 kgm magnesium sulphate, $48\frac{3}{4}$ kgm sodium chloride and silicic acid, are mixed, dried and heated, in a retort, to 400–650° C. The porous mass is again heated in vertical clay retorts and air passed through it. Chlorine is evolved, magnesium silicate and sodium sulphate remain.

3. The same mixture is treated with steam. When the disengagement of hydrochloric acid has ceased, the mixture is very strongly heated. Sulphuric acid distills off, and magnesia and sodium silicate remain.

4. Kainite, mixed with silicic acid, or silicates, is subjected to the same treatment; sodium sulphate, potassium sulphate, magnesium silicate and aluminate resulting.

5. Magnesium chloride solution, of 80–100° Twaddle, is mixed with 10 per cent. manganic oxide, heated to 44° C., and air passed through it. Chlorine is evolved continuously, if hydrochloric acid be added, as the magnesium chloride is decomposed. Addition of 25–30 per cent. calcium chloride, facilitates the process. (Method published previously by Clemm, Dingler's Polyt. Journ., **173**, 127.)

JOHN B. SPENCE, London: *Utilisation of metallic sulphides.* (Engl. P., No. 1855, May 9, 1879.)—Ores containing the sulphides of lead, zinc, iron, copper and silver, are to be finely pulverized, mixed with oil, and used as a "blue" paint. Or they may be calcined, treated with sulphuric acid, and again heated. Water dissolves out sulphates of zinc and copper, the latter to be precipitated from the solution by zinc. The oxide of iron is to be used as venetian red, after separating it from the lead and silver sulphates. The inventor also claims these methods of separation as new.

ACTIENGESELLSCHAFT CROIX, Croix. near Roubaix: *Improvements in the process of preparing hydrocyanic acid and its derivatives, from trimethylamine.* (Germ.P., No. 9409, September 27, 1879.)—Vapors of commercial trimethylamine are passed through vessels heated to redness, and then through sulphuric or hydrochloric acid, which absorbs ammonia. They are subsequently led to a tank, furnished with a stirring apparatus, and containing oxide of iron suspended in a solution of caustic potash. Yellow prussiate of potash is formed. From the condensers the unabsorbed illuminating gases are pumped to a gas holder.

THE AMERICAN CHEMICAL SOCIETY.

XX.—Proceedings.

Regular Meeting held May 6th, 1880.

The meeting was called to order at 8:30 P.M. Dr. A. R. Leeds in the chair.

In the absence of a quorum the regular business of the Society was deferred.

The Recording Secretary read a paper by Mr. Lucius Pitkin:

1. On "Some New Chlorobromoplatinates of Potassium."

In discussing Mr. Pitkin's paper, Dr. H. Endemann suggested that the compounds described were probably not chemical individuals, but mixtures of isomorphous salts.

The following papers were then read by their authors:

2. "On the Substituted Tolyl Compounds," by Jas. H. Stebbins, Jr., S.B.

3. "On a New Sulpho Acid of Phenanthrene," by Dr. Henry Morton and William E. Geyer.

4. "On the Action of Water and Argentic Hydrate on Benzine Hexachloride, and Naphthalene Tetrachloride," by Drs. Leeds and Everhart.

5. "Notice of the Discovery of Norwegium in American Lead," by Dr. Prochazka.

Fourteen members only being present, no regular business was transacted, and the meeting adjourned.

ARTHUR H. ELLIOTT,

Recording Secretary.

XXI.—The Chlorobromoplatinates of Potassium.

By Lucius Pitkin.

At the November meeting of the Society I described a new platinum salt, having the composition, $K_2PtCl_4Br_2$, which was called the chlorobromoplatinate of potassium. Since that time, however, I have found that this salt forms one of a series between the double chloride and the double bromide of platinum and potassium, the series comprising five compounds, each formed by the replacement of one or more atoms of chlorine in the double chloride, by a corresponding atom of bromine.

It will be remembered that in my previous experiments, the compound salt was formed by the action of potassium bromide on platinum tetrachloride, in the proper proportions; here, however, a different method was adopted, as, owing to the very rapid absorption of water, it was found impossible to accurately weigh out the platinic chloride. The method adopted was that of allowing a mutual reaction to take place between the double chloride, and the double bromide of platinum and potassium, by means of solution, digestion at a gentle heat, and cautious crystallization.

Both of these salts are easily prepared, are easily kept dry, and by weighing out the proper proportions, and allowing the reaction to take place under the conditions mentioned above, all the possible substitutions of Br for Cl, in this series of salts, are readily accomplished.

The five salts found, form connecting links between the double chloride, on the one hand, and the double bromide, on the other, and will be described in their order according to the number of Br atoms replacing the Cl; they are:

K_2PtCl_5Br, potassium monobromopentachloroplatinate.
$K_2PtCl_4Br_2$, potassium dibromotetrachloroplatinate.
$K_2PtCl_3Br_3$, potassium tribromotrichloroplatinate.
$K_2PtCl_2Br_4$, potassium tetrabromodichloroplatinate.
$K_2PtClBr_5$, potassium pentabromomonochloroplatinate.

Potassium monobromopentachloroplatinate, $K_2PtBrCl_5$. This salt, forming the first of the series of substitution products, differs very little in appearance from the double chloride of platinum and potassium. It can be most advantageously formed by the combination of five equivalents of chloroplatinate of potassium, with one of bromoplatinate, or by weight, 2444.0 parts of the former to 755.8 parts of the latter. In my experiments, 4.888 grms of the double chloride

were used, and 1.5116 of the double bromide. After solution, they were gently heated for some hours, and then allowed to crystallize, the solution being concentrated between each crystallization; by this means, six crops of crystals were obtained.

Three crops of the crystals were analyzed, the first, second and third, the last three being perfectly similar in appearance to those analyzed, all of which gave results very close to the theoretical amount calculated from the formula assigned.

The method of analysis consisted in ascertaining the amount of platinum in each crystallization, the salts being decomposed by heat and oxalic acid.

The theoretical percentage of platinum in this salt is 37.05, and the result of the three analyses were :

1st crystallization, 36.97 per cent.
2nd crystallization. 37.04 per cent.
3rd crystallization, 36.99 per cent.

The crystals of this salt were very small, under the same conditions which were favorable to the development of much larger crystals in the salts containing more bromine, and, throughout the course of these experiments, the tendency to form crystalline masses, of a size proportionate to the amount of bromine present, was well marked. The crystalline form of the salt is an octahedron, sometimes modified to a cubo-octahedron, while, under the microscope, a few frond-like masses of crystals were discovered.

Potassium dibromotetrachloroplatinate, $K_2PtBr_2Cl_4$. This salt has been already described, in full, in the November number of this JOURNAL (Vol. I, No. 11); a description will, therefore, not be necessary, except to say that, under the microscope, it exhibits the same general characteristics as the monobromated salt, with perhaps a greater abundance of the frond-like forms, this probably being due to a more rapid crystallization on the slide.

Potassium tribromotrichloroplatinate, $K_2PtBr_3Cl_3$. The salts of the series containing three, four and five atoms of bromine now remain to be considered. Heretofore, it was necessary to resort to fractional crystallization, in order to prove that the supposed salt was not a mechanical mixture; now, however, the crystallizations afforded such large crystals, that it could be readily perceived by the eye that such was not the case, and an analysis of only one specimen of each salt was rendered necessary.

The theoretical amount of platinum in this compound is 31.73 per cent., and an analysis yielded a result of 31.77 per cent., fully establishing the formula given.

It can best be prepared, as in the case of the monobromated salt, by combining potassium chloroplatinate with the corresponding bromoplatinate, in the proper proportions, which are, in this case, one equivalent of each, or by weight, 488 of chloroplatinate, to 755 of the bromoplatinate.

As thus prepared, it is a salt of a clear, reddish-yellow color, crystallizing readily in octahedra and cubo-octahedra.

Examined under a power of two hundred diameters (a drop of a solution, 1 : 50, being spontaneously evaporated for this purpose), it still showed, among the crystals of more definite form, frond-like radiations.

Potassium tetrabromodichloroplatinate, $K_2PtBr_4Cl_2$. Another salt, having the formula $K_2PtBr_4Cl_2$, has been formed like the preceding, but altering the proportions used. In this case, 4.5336 grms of the double bromide of platinum and potassium were used, while 1.4658 grms of the double chloride were employed.

The salt has a fine, bright, reddish shade, crystallizes easily, and, upon analysis, yielded 29.79 per cent. of metallic platinum—the calculated percentage being 29.61.

Potassium pentabromomonochloroplatinate, K_2PtBr_5Cl. This salt, the last of the series, exhibits a beautiful, ruby-red color, crystallizes in brilliant, and quite large, octahedra, and resembles, in great part, the ordinary double bromide of platinum and potassium, which it approaches closely in composition. An analysis resulted in showing a platinum percentage of 27.93, while the theoretical percentage was calculated as 27.76.

All of these salts are sparingly soluble in cold water, greatly more so in hot, and are precipitated from aqueous solutions by the addition of alcohol, while none of them are affected in the slightest degree by polarized light.

It is evident that the corresponding salts of the other alkaline bases can be formed in precisely the same manner, but limited time prevents a further investigation into the subject.

The supposition is also reasonable, and indeed, very probable, that more complicated substitutions can take place, involving a greater number of atoms ; for instance, the formation of a salt, such as $K_8Pt_4BrCl_{23}$, in which one bromine atom is substituted in a multiple of the empirical formula assigned to platinum and potassium double chloride.

In concluding, my thanks are due to Mr. Aschman, of the School of Mines, for instruments and assistance, in the part relating to the microscopic character of these salts.

School of Mines, Columbia College, February 9th, 1880.

XXII.—On the Substituted Tolyl Compounds.

By Jas. H. Stebbins, Jr., B.S.

In 1875, C. L. Jackson and Woodbury Lowry published an article in the *Berichte d. d. chem. Gesell.* (1875, 1672), entitled, "On Substituted Benzyl Compounds," and including the following substances:

Parabrombenzyl bromide, $C_6H_4Br—CH_2Br$. This substance was prepared according to the process indicated by Neuhof (Zeitschr. f. Chem., 1866, 653), for the preparation of chlorbenzyl chloride, namely, by passing bromine vapor into the vapor of boiling parabromtoluole. The boiling point rose, while the bromine vapors were being passed in, and copious fumes of hydrobromic acid were evolved. On cooling, the liquid crystallized into one solid mass, which, after being crystallized from boiling alcohol, showed a constant melting point. It crystallizes from alcohol easily, in long, white needles.

The brown, oily liquid accompanying these (probably a mixture of parabromtoluole and orthobrombenzyl bromide), crystallizes by slow evaporation, in large quadratic prisms. This substance possesses a pleasant aromatic odor, but the vapor irritates the eyes, and mucous membrane of the nose and mouth. It may be distilled with steam, but only very slowly. It sublimes easily, and burns with a green tinged, sooty flame. Insoluble in water, but pretty soluble in cold, and very soluble in warm alcohol. It is also soluble in ether, CS_2, $HC_2H_3O_2$ and toluole.

If heated with one molecule of $NaC_2H_3O_2$ and absolute alcohol, in a flask connected with a reflux condenser, sodium bromide is precipitated out, and a thick liquid is obtained, possessing a pleasant odor. If this substance be heated with CuO, it will burn with a green flame. This body was, therefore, looked upon as a brombenzyl-acetate.

Metabromtoluole, prepared according to Wroblewskey's method (Ann. Chem. Pharm., **168**, 153), on being treated with bromine vapor, yielded likewise a liquid, the smell of which differed considerably from that of the preceding substance, but it attacked the eyes and nose in the same way. Treated with $NaC_2H_3O_2$ and absolute alcohol, a bromoacetate was likewise obtained.

The orthobromtoluole, treated in the same way, yielded orthobrombenzyl bromide.

In 1877, C. L. Jackson and Woodbury Lowry (Ber. d. d. chem. Gesell., 1877, 1209) published their second paper, entitled, "On Parabrombenzyl Compounds," and add that parabrombenzyl bromide

may likewise be prepared by treating benzyl bromide, in the cold, with bromine and a little iodine; but they found that this method is far inferior to the one at first described. Farther on they describe a few more compounds, obtained from parabrombenzyl bromide, which I will now repeat, as I shall, later on, have occasion to refer to them.

Parabrombenzyl alcohol, $C_6H_4Br—CH_2OH$. This was prepared by heating parabrombenzyl bromide for several days (in a flask connected with a reflux cooler), with water, until the eyes were no longer attacked. It was also prepared from parabrombenzylacetate, by heating to 150°, with aqueous ammonia. The alcohol appears as long, flat and elastic needles, with pearly lustre and disagreeable odor —melting point, 69°—and may be distilled in a current of steam.

Parabrombenzyl cyanide, $C_6H_4BrCH_2.CN$, was prepared by boiling parabrombenzyl bromide with an alcoholic solution of KCN.

Parabromalphatoluylic acid, $C_6H_4BrCH_2COOH$, was prepared from the foregoing, by heating it in sealed tubes, with hydrochloric acid, to 100°.

Alcoholic ammonia acts readily on parabrombenzyl bromide, at the ordinary temperature, forming a crystalline mass, which is nearly insoluble in alcohol. This mass consists of two substances, one crystallizing in leaflets, and the other in needles. The latter showed itself to be triparabrombenzylamine, $(C_6H_4BrCH_2)_3N$.

These compounds seemed to be of so interesting a nature, that I had for some time contemplated the idea of working on them; but for fear of infringing on Prof. Jackson's work, the idea was dropped, until recently, when I determined to experiment on the substituted tolyl compounds, which seemed to offer a large and unexplored field to work upon.

As xylole is the next higher homolgue to toluole, it seemed but natural that I might reproduce all of the compounds detailed in the beginning of this paper, with the difference of containing the tolyl, instead of the benzyl radical. With this point in view, I proceeded as follows:

I first prepared my bromxylole, by treating one mol. of commercial xylole (surrounded with cold water), with four atoms of bromine, which were allowed to flow in drop by drop.

During the operation, copious fumes of HBr were evolved, and the oily liquid was then washed with water made alkaline with KOH, so as to absorb all traces of HBr and Br.

It was then thoroughly washed with distilled water, and, after being mixed with a few pieces of $CaCl_2$, placed under the air pump to dry.

The oil thus obtained, when perfectly dry, is clear, and possesses a light yellow color. It boils at 197°.25, instead of 204°, which is the boiling point for metabromxylole, thus showing that it is a mixture of the meta and parabromxylole, the former predominating. The reaction here taking place, may be expressed as follows:

$$C_6H_4(CH_3)_2 + 2Br_2 = C_6H_3Br(CH_3)_2 + HBr.$$

Action of bromine on metabromxylole.—There are two methods of bromizing; one, already indicated by Jackson, by passing a stream of bromine vapor into the vapors of boiling metabromxylole; and the other, by allowing a small stream of bromine to fall gradually into metabromxylole, heated from 135–140°. This method was also tried by Jackson and Field, with far better results than with the previous one.

The proportions used were respectively, 10.3 grms metabromxylole and 17.7 grms bromine. The two substances were mixed, as already stated, and heated in an oil bath, from 135–140°. The heating lasted about four hours, and, during this time, copious fumes of HBr were given off, thus showing that the substitution in the side chains was taking place freely.

The result was a black, thick oil, with a strong odor resembling parabrombenzyl bromide, and likewise attacking the eyes and nose, though not so strongly as the latter.

It was poured on a large watch glass to cool, and placed under the air pump, in the hope that by so doing it would crystallize; but several days standing produced no result. It was therefore supposed that the substance was not pure, but might be a mixture of the para and meta combinations, and that by submitting the raw material to distillation in a current of steam, the more volatile of the two combinations would distill over, while the less volatile would remain behind. This supposition was fully verified, for, no sooner had steam begun to pass through the solution freely, than a clear, light colored oil began to distill over. The distillation is slow, and it was some time before all the oil had passed over. This light colored oil has a pleasant, aromatic odor, and attacks the eyes and nose very strongly. It is easily soluble in hot alcohol, but, on cooling, separates out in oil drops again.

This oil is probably the metabromtolyl bromide, and, as the corresponding metabrombenzyl bromide is a white crystalline body, it seemed strange that it should not crystallize. After trying several methods to obtain it in a crystalline state, without success, I became discouraged, and placed the oil away under the air pump for several

days. When I again looked at the oil I was greatly surprised, for it was filled with pretty little white crystals, showing that the oil only required time to crystallize.

The black oil remaining in the distilling apparatus is probably the parabromtolyl bromide, which I have not yet had occasion to examine.

The reaction taking place here, may, I think, be expressed in the following equation :

$$C_6H_3Br(CH_3)_2 + 2Br_2 = C_6H_3Br\begin{cases}CH_2.Br\\CH_2.Br\end{cases} + 2HBr.$$

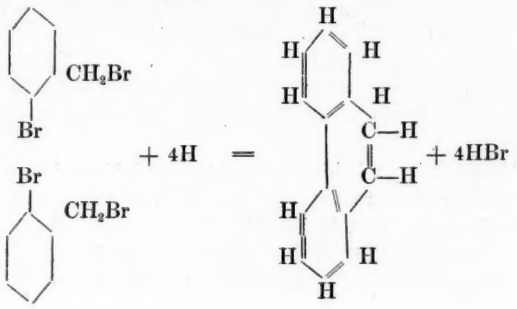
I have not had time to investigate this substance more extensively, but I propose next fall to include among my experiments all of Jackson's compounds, and study each one individually.

In 1879 (Ber. d. d. chem. Gesell., 1965), Jackson and White published an article describing the synthesis of anthracene, by acting on orthobrombenzyl bromide with metallic sodium.

In carrying out their experiments, they treated a dilute solution of orthobrombenzyl bromide, in ether, with small pieces of sodium, and heated gently. A violent reaction took place, and in a short time the smell of the orthobrombenzyl bromide disappeared. The mixture thus obtained, was distilled with water, the distillate separating into three layers. The substance collected in the distilling tube, has a strong smell of anthracene, and was found to be bihydrated anthracene, which, upon being treated with strong H_2SO_4, in the water-bath, yielded pure anthracene, melting at 213°.

This demonstrates that the two C atoms in anthracene, stand in relation to the two benzole nuclei, in the 1 : 2 position.

The formation of anthracene may be represented as follows, whereby it will be seen that two mols. of orthobrombenzyl bromide unite with one another, giving off HBr, viz.:



In the same way, I hope to arrive at the constitution of pyrene, which is $C_{16}H_{10}$, only, in this case, I am not certain what position the carbon atoms hold, and will, therefore, have to try all the three bromtolyl bromides. If we combine two molecules of, say, metabromtolyl bromide, and treat the mixture with sodium, we should get a bihydrated pyrene, and this, treated with H_2SO_4, should yield pure pyrene.

XXIII.—On a New Sulpho Acid of Phenanthrene.

By Henry Morton and William E. Geyer.

A monosulpho acid of phenanthrene was first prepared by Graebe,* and subsequently by Rehs.† Graebe heats phenanthrene with its own weight of oil of vitriol, for some time, on the water-bath. Rehs uses slightly fuming acid, apparently at ordinary temperatures.

Merz and Weith‡ have shown that when naphthalene is heated with sulphuric acid, at 100°, α-naphthalene sulpho acid is the main product, but if the temperature is raised to 160–170°, the β modification is almost exclusively formed. We have found that in the same way, phenanthrene, also, forms two distinct monosulpho acids. That formed according to Graebe's method, we propose to call the α-acid, ours the β-naphthalene sulpho acid.

To serve as a means of comparison, we first prepared the α-acid. The process is simple, but the yield is small, the greater part of the phenanthrene remaining unattacked. To prepare the β-acid, three parts of phenanthrene were heated with two parts of sulphuric acid, in a paraffine bath, to 170°, for three hours. Towards the end, the temperature was, for a short time, raised to 190°. Much vapor of water and sulphurous acid were given off, during the entire time of heating. On cooling, there was obtained a very black, tenacious pitch. This, with the exception of a little unaltered phenanthrene, dissolves in water to a very dark greenish-black liquid. When this liquid is much diluted, heated to boiling, and neutralized with lead carbonate, the black coloring matter is completely carried down with

* Ann Chem. u. Pharm., **167**, 152.
† Ber. d. d. chem. Gesell., **10**, 1252.
‡ Ber. d. d. chem. Gesell., **3**, 195.

the lead sulphate, and, on filtering hot, we obtain at once an almost colorless liquid, from which, on cooling, a nearly pure lead salt of the β-acid separates. By long continued digestion with boiling water, it can be redissolved and purified by recrystallization. The finely divided salt is suspended in water, and treated with sulphuretted hydrogen. On evaporating the filtrate from the lead sulphide, we obtain a thick syrup, which soon crystallizes. The yield is small; we have not yet had time to vary proportions, temperature, and time of heating, to ascertain the best conditions.

β-phenanthrene sulpho acid crystallizes in fine, white needles, with a strong, pearly lustre. It is greasy to the touch, very soluble in water and alcohol, but not deliquescent. Its salts are much less soluble than the corresponding α-salts. It is a powerful acid, displacing, for instance, chlorine, and precipitating its own salt when a solution of the acid is added to a solution of the chlorides of potassium, sodium, ammonium, barium, calcium, zinc, copper, etc.

Lead salt: $(C_{14}H_9SO_3)_2Pb + 3H_2O$, obtained in indistinctly crystalline crusts, on evaporating the solution. After drying between blotting-paper, its weight in the air is constant. 2.494 grms, dried at 155–160°, lose 0.173.

	Calculated for $3H_2O$.	Found.
H_2O,	6.96 per cent.	6.93 per cent.

0.460 grm of the salt, dried at 160°, gave 0.193 $BaSO_4$.

	Calculated for $(C_{14}H_9SO_3)_2Pb$.	Found.
Pb,	28.71 per cent.	28.66 per cent.

Barium salt: $(C_{14}H_9SO_3)_2Ba + 3H_2O$, obtained by nearly neutralizing a boiling solution of the acid with barium hydrate. On cooling, the salt separates in brilliant scales, often grouped in rosettes. If the solution is not acid, the salt is apt to separate in light, fungoid growths, of indistinct crystals.

	Calculated for $3H_2O$.	Found.		
		I.	II.	III.
H_2O,	7.65 per cent.	7.50	7.81	7.58 per cent.

Dried at 160°.

	Calculated for $(C_{14}H_9SO_3)_2Ba$.	Found.
Ba,	21.04 per cent.	20.90 per cent.

Air dried.

	Calculated for $(C_{14}H_9SO_3)_2Ba + 3H_2O$.	Found.
Ba,	19.43 per cent.	19.30 per cent.

Potassium salt: brilliant plates; do not lose weight at 180–190°.
Ammonium salt: same appearance as potassium salt.

Zinc salt: white plates.
Copper salt: beautiful, very light green needles.
Nickel salt: light green plates.
Cobalt salt: flesh colored plates.

β-PHENANTHROL.

The potassium or sodium salt of β-phenanthrene sulpho acid, on fusion with potash, yields readily a phenol-like body, $C_{14}H_9OH$. From petroleum benzine it can be obtained in crystals. It dissolves readily in alkalies, is reprecipitated by acids, is very little subject to change on exposure to air, and in alkaline solution unites with diazo bodies generally. The compounds formed with the diazo derivatives of sulphanilic acid, of napththionic acid, and of the sulpho acid of an amido phenanthrene, are dye-stuffs, differing much in shade from the corresponding compounds of α-phenanthrol. These bodies are still under investigation.

XXIV.—On the Action of Water and of Argentic Hydrate upon Benzine Hexachloride and Naphthalene Tetrachloride.

By A. R. Leeds, Ph.D., and E. Everhart, Ph.D.

Before passing to a description of the results obtained, it is important to describe certain modifications in the methods of preparing the benzine hexachloride and naphthalene tetrachloride, which have yielded unexpectedly good resnlts.

I. PREPARATION OF BENZINE HEXACHLORIDE.

The original mode of preparing benzine hexachloride, was by the exposure of benzine to an atmosphere of chlorine.* Subsequently it was stated by Heys,† that it was obtained most readily by acting on boiling benzine with excess of chlorine. This method was accordingly made use of in the first instance. The benzine was introduced into a flask heated over a water-bath. A stream of dry chlorine was sent into the flask, the excess passing off through a tube surrounded by a condenser. The exit tube was made to dip below the surface of water. After the chlorination had been continued for eighteen hours, a few drops of an oily liquid had collected beneath

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*Mitscherlich, Pogg. Annal., **35**, 374; Péligot, Ann. Chem. Phys. [2] **56**, 66; Laurent, Ann. Chem. Phys. [2], **63**, 27.

†Zeitschr. f. Chem. [2], **7**, 293.

the surface of the water. The operation was then interrupted, the unaltered benzine distilled off, the residue washed with ligroine, and crystallized out of alcohol. The product obtained in this manner was so very small (only approximately 5 grms of the hexachloride from 100 grms benzine), that the process was abandoned.

The chlorination was then performed in the sun-light, the benzine being introduced into a tall two gallon bottle, of white glass, and the stream of chlorine flowing down through a wide glass tube ending just above the surface of benzine. The experiment was a very striking one. The interior of the bottle at once becomes filled with dense white clouds, the temperature of the benzine rises from the energy of the reaction, and presently the liquid becomes turbid, and precipitation of a white crystalline product ensues. After sixteen hours exposure, 600 grms benzine yielded 350 grms hexachloride, the bottom and sides of the bottle being covered with crystals of the almost pure product. On recrystallization from alcohol or benzine, they yielded after the third crystallization, rhombic crystals of great beauty, with a definite melting point (157°). The unaltered benzine was distilled off from the liquid portion, and, after allowing the residue to crystallize as far as it would, and washing with cold alcohol, it was thrice recrystallized out of alcohol or benzine, as above. This part of the process yielded the main portion of the benzine hexachloride obtained, the melting point of the product obtained after the third recrystallization always standing at 157°.

The residues extracted by alcohol were of a dark red color, and of an oily consistence. They were divided into two portions, *A* and *B*.

A was treated with an excess of water, and washed six times with the same. The undissolved oily matters were then treated repeatedly with cold ligroine. This dissolved out all the oil, and left behind on the filter, a white substance, soluble in alcohol and benzine. After recrystallization from alcohol, the melting point was found to be 157°, and the substance was benzine hexachloride.

The oily portions insoluble in ligroine, were purified by repeated washing with the same. From the final solutions, the ligroine was expelled by exposing them to a temperature of 65° for several days, and, finally, by heating on a water-bath, until the weight became constant. This yielded a heavy, dark red oil, which was set aside in a cold place for six months, in order to see whether any dissolved crystalline substance would crystallize out. Such proved to be the case, and at the expiration of this long interval, a small crop of crys-

tals of benzine hexachloride was obtained. The main portion was then treated with alcoholic potash. On distilling, α-trichlorbenzine, $C_6H_3Cl_3$, came over, and the residue boiled at 179°, and proved to be orthodichlorbenzine, $C_6H_4Cl_2$.

B was submitted to distillation. After the alcohol was driven off, the temperature rose quite rapidly, until the thermometer stood at 200–210°. Between 110° and 190° nothing came over except a small quantity of oil. At a higher temperature decomposition set in, as was shown by the hydrochloric acid fumes, and a pale yellow oil, accompanied by volatilized benzine hexachloride, distilled over. After removing the oil from the distillate by washing with ligroine, the solid residue was recrystallized from alcohol, and afforded crystals which, by their melting point of 157°, were proven to be benzine hexachloride. The ligroine was expelled from the oily portion by heating to about 65° for several days, at the end of which time, long, white needle-shaped crystals of α–trichlorbenzine separated out. Their melting point was 17°.

II. PREPARATION OF NAPHTHALENE TETRACHLORIDE.

Instead of passing a rapid stream of chlorine over naphthalene, as was done by Laurent, Faust and Saame made the dry chlorine to flow in a rapid stream into fused naphthalene until the mass assumed the consistency of butter, on cooling.* These methods were rejected. by E. Fischer,† on the ground that the chlorination can never be carried to so high a stage by means of dry chlorine, as it can be by the action of potassium chlorate and hydrochloric acid, in the manner which he has described. He attributes this to the viscous condition into which the chlorinated mass eventually passes when dry chlorine is used, and which prevents further action. And the warming of this mass to render it fluid must be avoided, lest, as Laurent, Faust and Saame, and others have pointed out, an increased production of secondary products should occur. Fischer modified the process, which was originally proposed by A. and E. Depouilly,‡ in so far as he intimately mixed the naphthalene with the calculated amount of potassium chlorate, by pulverization in a mortar. Enough water was then added to allow the mass to be rolled into balls which, after drying, were porous and firm. After being subjected to the action of con-

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*Naphthalene Derivatives, Ann. der Chem., **160**, 65; Zeitschr. f. Chem. [2], 5, 705.

†Ber d. d. chem. Gesell., **11**, 735.

‡Bull. Soc. Chim., **4**, 10.

centrated hydrochloric acid, none of the naphthalene remained unaltered.

This method was found by the authors to give a somewhat larger product than that of Faust and Saame (the naphthalene tetrachloride obtained amounted to fifteen per cent. of the naphthalene employed), but to be excessively troublesome and unpleasant. A very large amount of a dark red oil was formed at the same time, the complete separation of which, by means of pressure, etc., was difficult, and the preparation of any considerable amount of pure naphthalene tetrachloride, by this method, most tedious.

The plan adopted by the authors, was to expose as large a surface as possible of the naphthalene, to the action of direct sun-light, in an atmosphere of chlorine. To this end a chlorinating chamber was arranged, which will be found convenient in similar cases where sun-light is to be used. A large bell-jar, placed in a porcelain tray, was closed by a cork through which three tubes were passed, the cork being protected from the action of chlorine, by plaster of Paris poured in so as to form a solid cap on the under side. One of the tubes, serving as an exit, was connected with a Peligot tube partially filled with water, so as to detain any volatile products of chlorination.

The other two were connected with large chlorine generators. Gallon bottles, partly filled with roughly powdered black oxide of manganese, and placed in tall tin boilers containing water kept at the boiling point, were found to be the most convenient arrangement. The hydrochloric acid was poured into the bottles through safety funnels, and the chlorine dried by passage through a sulphuric acid wash bottle. Such an arrangement would keep a continuous stream of chlorine flowing for an entire day, with no attention other than that of the occasional addition of acid. The naphthalene was contained in five shallow glass dishes, piled up one above another, with separating strips of kerite between. The absorption of a rapid stream of chlorine under these conditions was so energetic, that a constant pressure inward was produced. The interior became filled with dense white clouds, and the sides of the jar coated with a whitish-yellow, oily mass. In one chlorination, from 415 grms of naphthalene used, 185 grams, or 45 per cent., of tetrachloride, were obtained. When the absorption of chlorine ceased, the oily mass was scraped into a capacious flask, and treated four times with boiling ligroine. This removed most of the oily naphthalene dichloride, $C_{10}H_8Cl_2$. The ligroine extract, *A*, was set aside for further examination.

The portion insoluble in ligroine was treated two or three times with boiling alcohol, which removed the last traces of the oil, and left the residue almost perfectly white. This, after recrystallization from chloroform, yielded very large and beautiful monoclinic prisms of pure naphthalene tetrachloride, $C_{10}H_8Cl_4$, m. pt., 182°. The products obtained from the alcoholic extract, *B*, are given below.

The extract *A*, after standing for a number of hours, deposited a large, solid mass, which, after filtration and draining, was washed four or five times with small quantities of alcohol, until it became white. This dissolved in chloroform, in which it is readily soluble, and crystallized out in long prisms. The successive crystallizations from chloroform were dissolved in ether, and yielded, on repeated recrystallizations, the same long, prismatic needles of monochlornaphthalene tetrachloride, $C_{10}H_7ClCl_4$; m. pt., 128°.

The alcoholic extract, *B*, after being distilled to small bulk, deposited, on standing, a heavy crystalline mass which, after washing with alcohol and crystallization from ether, in which it dissolved with difficulty, proved to be naphthalene tetrachloride. The melting point of the crystals thus obtained was 182°. The mother liquor, on standing, gave a further deposit which, after repeated crystallizations, first from alcohol and then from acetic acid, proved to be prisms of dichlornaphthalene tetrachloride, $C_{10}H_6Cl_2Cl_4$; m. pt., 172°. It had been hoped that they would prove to be the *β* modification of naphthalene tetrachloride announced by Laurent. A further proof, if that had been needed, that they were not, was, that on treatment with alcoholic potash, they yielded silky needles of tetrachlornaphthalene, $C_{10}H_4Cl_4$, with a melting point of 130°.

III. ACTION OF WATER AND ARGENTIC HYDRATE UPON BENZINE HEXACHLORIDE.

After treatment of benzine hexachloride with water for a number of days, in sealed tubes, at a temperature of 200°, a dark mass was obtained which, on examination, proved to be chiefly unaltered hexachloride, with a little tarry matter. The latter yielded no crystallizable body on appropriate treatment.

Four sealed tubes, each containing fifteen grms benzine hexachloride and eighteen grms argentic hydrate, were heated in an oil-bath to 200°, for eighty hours. On opening the tubes, there was a strong outward pressure of a gas which proved to be carbonic acid. After removing the supernatant liquid, which contained much hydrochloric acid, it, and the aqueous extracts obtained on repeated washing, were evaporated to dryness. A tarry mass was obtained, from

which no crystalline substance could be derived, either by solvents, or by distillation or sublimation.

The residue, insoluble in water, proved to be merely unaltered benzine hexachloride and argentic hydrate. On distillation it yielded hydrochloric acid, benzine hexachloride, and a small amount of trichlorbenzine, arising from the decomposition of a portion of the hexachloride.

These negative results were highly disappointing, since the anticipation had been that a substitution of hydroxyl for chlorine would occur, giving rise to hydroxylated addition products, similar to, or identical with phenose, $C_6H_6(OH)_6$.

IV. ACTION OF ARGENTIC HYDRATE UPON NAPHTHALENE TETRACHLORIDE.

Four sealed tubes, each containing twenty grms of naphthalene tetrachloride and fifteen grms of argentic hydrate, the two substances being intimately mixed previous to their introduction into the tubes, were heated in the oil-bath to 200° C., for eight hours a day, during an interval of three weeks. During the first few days, the small amount of water used in transferring the materials to the tubes, and floating above the solid matters at the bottom, assumed a light reddish tinge, but afterwards it became lighter and lighter, until finally, when the tubes were removed, it had become entirely colorless. On opening, there was a strong pressure outwards of carbonic acid. The contents consisted of two portions, a solid, tarry mass, and a colorless liquid, strongly acid from the presence of free hydrochloric acid. The solid portion was repeatedly washed with water, filtered, and the filtrates added to the original aqueous extract. The whole was then evaporated to dryness, and heated in a subliming chamber to 194°, at which temperature, very beautiful, long, silky white needles came off. The needles melt at 130°.

0.2249 grm of the substance yielded 0.5324 grm CO_2, and 0.0639 grm H_2O.

0.2229 grm yielded 0.1784 grm AgCl.

This would agree more nearly with the composition of monochlornaphthol, $C_{10}H_6ClOH$, than with any other derivative of this class.

	Found.	Theory.
Carbon	64.56	67.22
Hydrogen	3.16	3.92
Chlorine	19.78	19.88
Oxygen	12.50	8.98

On recrystallization from alcohol, its melting point sank to 112°. This shows that the sublimed needles were probably accompanied by the dichlornaphthyhydreneglycol, which has a melting point of 155–156°. But the small amount of the substance obtained, and the unfortunate bursting of very many sealed tubes, prevented the repetition of the analysis.

The decomposition of naphthalene tetrachloride, by the action of water at high temperatures, has previously been studied by E. Grimaux. In his earlier work,* Grimaux found that by the combined action of water at 200–210°, a substance was obtained which was soluble in hot water, from which it separated in small crystals, melting at 142°. He assigned to this body the formula,

$$C_{10}H_8Cl_2\begin{cases}OH\\OH\end{cases}$$

Later he recognized the substance as a glycol,† the twice chlorinated naphthyhydreneglycol, and stated that it crystallized in shining tables, melting at 155–156°. By the action of boiling hydrochloric or hydrobromic acid upon this compound, there distills off along with the steam, a body which, according to its composition and its reactions, is the once chlorinated naphthol, $C_{10}H_6ClOH$.

It crystallizes in long colorless needles, melting at 109°. By oxidation of the new glycols, phthalic acid only was obtained. But indirectly, by boiling naphthalene tetrachloride with a solution of argentic nitrate or with dilute nitric acid, Grimaux obtained an oxidation product crystallizing in hexagonal tables, and with a composition corresponding to the formula, $C_{10}H_8Cl_2O_2$. Its melting point was 195–196°.

The solid portion was repeatedly digested with alcohol. On distilling the alcoholic extracts, a blackish, oily residue remained, which was subjected to further distillation by heating the body of the retort in an air-bath. On raising the temperature, there was some disengagement of hydrochloric acid, due probably to the decomposition of a small amount of unchanged naphthalene tetrachloride, which had gone into the alcoholic solution. Up to 280° there was no constant temperature, although a thin, transparent oil was given off, from which crystals soon began to separate. After freeing these crystals as much as possible from the accompanying oil, by pressure between filter paper, they were crystallized again out of hot alcohol. The crystals proved to be the same as the main portions of the sublimate,

* Berl. Ber., 5, 391.

† Ber. Ber., 5, 827.

which came off at about 280°. After recrystallizing this a number of times from hot alcohol, crystals were obtained having a constant melting point of 120°.

They are insoluble in water, slightly soluble in cold alcohol, readily soluble in hot alcohol and in ether. They are in the form of extremely thin, transparent, colorless leaves. While separating rapidly from hot alcohol, these films exhibit magnificent prismatic tints, and present more or less of rhombic outlines, the edges of the rhomb being frequently as much as 0.5 cm in length. On sublimation, the crystals are deposited in beautiful white leaves of the same form and of a pearly lustre.

0.2974 grm yielded on analysis 0.6603 grm CO_2, and 0.0978 grm H_2O.

0.3708 grm yielded 0.5104 grm AgCl.

These results would make the substance a modification of dichlornaphthalene, $C_{10}H_6Cl_2$.

	Found.	Theory.
Carbon.....	60.65 per cent.	60.91 per cent.
Hydrogen..	3.29 "	3.04 "
Chlorine.....	36.20 "	36.05 "

But in its properties, this substance is entirely different from the two isomeric modifications of dichlornaphthalene, which, up to the present time, have been the only two that have been obtained directly from naphthalene tetrachloride. These two are the α, obtained by the action of alcoholic potash, and forming a crystalline mass, melting at 35–36°, and the β, obtained when small quantities of the tetrachloride are rapidly distilled, and forming colorless prisms, with a melting point of 68°

Neither does it correspond with the other five modifications, which have been previously described, and which, it must also be remembered, are derived in an entirely new manner. They are:

γ. Obtained by acting upon α-dinitronaphthalene with phosphoric chloride, and by the passage of chlorine through melted naphthalene, and distilling the product. It forms colorless, brilliant crystalline scales, with a melting point of 107°.

δ. By heating α-naphthalenedisulphochloride with phosphoric chloride; it forms colorless leaves, with a melting point of 114°.

ε. From β-naphthalenedisulphochloride, in like manner; shining prisms, with melting point at 135°.

ζ. By acting upon β-dinitronaphthalene, with phosphoric chloride; large, rhombic crystals; m. pt., 83°.

η. By heating nitronaphthalenesulphochloride (obtained from β-naphthalenesulpho acid) with excess of phosphoric chloride; colorless needles; m. pt., 48°.

The only one of these which resembles in characters the one formed from the naphthalene tetrachloride, in sealed tubes, is the δ modification, but its melting point, as will be seen, is considerably lower. For these reasons, the modification described must be regarded as new, and to it, which is the eighth now known, we shall accordingly give the name ϑ–dichlornaphthalene.

XXV.—On the Probable Occurrence of Norwegium in American Lead.

By Geo. A. Prochazka.

C. W. Blomstrand reports (Ber. d. d. chem. Gesell., **12**, 1731) on the discovery of norwegium by Tellef Dahll, substantially as follows:

"On a small island, Oterö, in the neighborhood of Kragerö, where Mr. Dahll resides as mining director, towards the end of the year 1878, a calcite gangue, interspersed with small particles of copper, nickel and nickel glance, was discovered. The nickel glance, on analysis, gave nickel, cobalt, iron, arsenic and sulphur. The hydrogen sulphide precipitate was treated with ammonium sulphide to remove the arsenic; the black sulphide of a new metal remained undissolved. 10 kgrms of the ore were then roasted; the residue was dissolved in acid and precipitated by H_2S. The precipitate was dried and again roasted; the oxide thus produced was reduced to metal.

Further investigation proved that the metal contained copper. To remove the copper the metals were converted into chlorides, and the solution diluted with a large excess of water. The new metal was thereby precipitated as oxichloride, while copper remained in solution. The new metal in its properties bears very close resemblance to bismuth.

	Bismuth.	Norwegium.
Melting Point	264°	254°
Atomic Weight (R_2O_3)	210	218.9
Sp. Gravity	9.8	9.441

The oxides of both metals are fusible, and give in the flame, on porcelain, a metallic mirror. The main difference between the two metals consists in the solubility of the oxihydrate of the new metal in caustic alkali, as well as in ammonium and sodium carbonate solution, on boiling. The difference is well marked if carbonates are treated in the same manner.

In the course of an examination of American refined lead, containing comparatively large quantities of copper and nickel, the bismuth had been precipitated in the ordinary manner by an excess of sodium carbonate, from the potassium cyanide solution of the 5th group of metals (Fresenius). In the alkaline filtrate, H_2S produced a reddish-brown precipitate, which could not be identified as the sulphide of any of the well known heavy metals. It was readily soluble in dilute nitric acid. From this solution a basic salt was precipitated by water. Potassium carbonate produces a precipitate which is soluble in an excess of the boiling precipitant. Hydrogen sulphide precipitates the original sulphide from the alkaline solution.

The quantity of sulphide was very small, amounting to about 1 mgrm from 200 grms of lead.

The reactions, as far as they could be verified, considering the smallness of the quantity of material, correspond to the description of norwegium as given by Dahll.

The refined lead was a mixture of leads from various sources, but it is not improbable that there may be a connection between the presence of copper, nickel and norwegium. Proper attention given to the various lead ores, especially those which yield lead containing larger quantities of copper and nickel, will undoubtedly throw further light upon this subject.

The results obtained seemed of sufficient interest for publication for the benefit of those who may be more favorably situated, both with regard to time and material, than I am at present.

XXVI.—On Chicken Cholera: Study of the Conditions of Non-recidivation and of Some Other Characteristics of this Disease.

By M. L. Pasteur.*

Translated from the *Comptes Rendus de l'Academie des Sciences*, of April 26th 1880, page 952, by P. Casamajor.

In the communication which I had the honor of presenting to the Academy in the month of February last, I announced, among other results, that chicken cholera originates in a microscopical parasite; that there is an attenuated virus of this disease, and that one or more inoculations of this attenuated virus may preserve chickens from death when inoculated with the virus of maximum virulence. On account of the striking similarity that these two forms of virus present with the effects of variola and vaccine in man, it becomes in-

* The translation of the first paper of this series appeared in this Journal, February, 1880 (**2**, 79).

teresting to ascertain not only if the immunity from the more aggravated form of virus is absolute, for the regions of the body which have undergone the preventive inoculation, but also if this immunity exists in the system, no matter what portion of the animal may have been inoculated, and what may have been the manner of introducing the virus.*

To explain with brevity the results which I have to communicate, I may be allowed to use the word *vaccinate*, to express the act of inoculating a chicken with the attenuated virus. This being admitted, I may state, as the result of many experiments, that the effects of vaccination are very variable. Some chickens are little affected by the most virulent virus after one inoculation of the attenuated virus; others require two such inoculations, and even three. In every case, the preventive inoculation does some good, because it acts in a certain measure. Vaccination, then, may be of several degrees; but we may always succeed in completely vaccinating a chicken, which means that we can bring it to such a condition that it becomes incapable of being affected by the most virulent virus.

To make this matter clear, I will now give the results of experiments: I take eighty new chickens (I call *new* those which never suffered before with chicken cholera). On twenty of these, I inoculate the most virulent virus—and they all die. Of the sixty that remain, I take another lot of twenty, and I inoculate them with that quantity of the most attenuated virus which the point of the needle will take up †— and not one dies. Are they then vaccinated for the aggravated form of virus? Some are and some are not, for if I afterwards inoculate these twenty chickens with the most virulent virus, six or eight of them will not die, although they may be ill, while in the first case every inoculated chicken died. I take again from the remaining chickens another lot of twenty, and these are vaccinated with the attenuated virus exactly as the preceding lot, and, a week afterwards, they are again vaccinated in the same manner. Are they now safe from the virulent virus? We now inoculate these twenty chickens with this virulent virus, and, instead of there being six or eight which do not die, there are twelve or fifteen. Finally, I take the twenty remaining chickens, and vaccinate them suc-

*From all I have seen and read of vaccine in man, and from my experiments on chicken cholera, I infer that *vaccine* rarely acts as a complete preventive. There are cases cited, of vaccinated persons who have had the variola, and there are even cases of persons who have had it, afterwards, as much as three times.

†There are degrees of attenuation as well as of virulence. I will give explanations in a future communication.

cessively three or four times. If now I come to inoculate them with the most virulent virus, not one will die. In this case, chickens are brought to the condition of animals who are incapable of suffering from chicken cholera.

As to the cause of non-recidivation, I find it impossible to resist the idea that the microscopic germ, which causes the disease, finds in the body of the animal conditions suitable to its development, and that to satisfy the necessities of its life, the germ alters certain substances, or destroys them, which comes to the same thing, whether it assimilates them, or whether it consumes them with oxygen borrowed from the blood.

When complete immunity has been reached, the most virulent germ may be inoculated into any of the muscles without producing any effect. This means that the cultivation of the germ has become impossible in these muscles. They no longer contain food for the germ.

It is impossible to convey the impression that one receives from observing such phenomena. Here are twenty chickens which never had this disease. I inoculate them in their pectoral muscles or, still better, in the muscle of the thigh, so as to observe with greater ease the effect of the inoculation. The next day all the chickens are lying down ; they are very lame and seem overcome by sleep. The inoculated muscle becomes of enormous size and is profusely filled with the parasites. From time to time, a chicken dies, and, at the end of forty-eight hours, they are all dead. We may take also twenty chickens, previously vaccinated several times, and inoculate them at the same time as the others, with the same virus, in equal quantities. The next day and the next, they are all alive and in good health ; they eat and cackle as usual ; the cocks crow ; the inoculated muscles present nothing abnormal. There is not even a sign to show where the skin was punctured. This healthy condition remains permanent.

We may now inquire whether the impossibility of cultivating the parasite is not limited to the muscles which have been inoculated. This may be answered by introducing the deadly virus in the blood vessels and in the digestive organs. I have taken ten chickens, never before inoculated, and ten others inoculated several times with the mild virus. I have then injected the worst form of virus in the jugular vein of all these chickens. The first ten have died rapidly ; many of them within twenty-four hours. The ten vaccinated chickens, on the contrary, have only been slightly ill from the

incision of the skin and of the jugular vein, and were soon in good health. This shows that the blood of these ten chickens was itself *vaccinated*, which means that previous cultivation had deprived it of the materials fit for further developments of the germ.

As to the introduction of the parasite in the digestive organs, I have imitated the epidemics which depopulate poultry yards, by introducing the parasite in the food of the chickens. On the 11th of March, I brought together twelve chickens, bought at the market that very morning, and twelve others, previously vaccinated several times. Every day I gave to these twenty-four chickens a meal of the diseased muscles of chickens, who had died from chicken cholera. Through the combs of the twelve chickens which had not been vaccinated, I passed a platinum wire, so as to distinguish them from the other twelve. On the next day, the unvaccinated chickens began to sicken and die. On the 26th of March, the experiment terminated. Seven of the chickens that had not been vaccinated have died, and a *post mortem* examination reveals the fact, that the disease was introduced in the system, either through the first portion of the alimentary canal, or more frequently, through the bowels, which were highly inflamed, and sometimes ulcerated, in a manner which recalls the lesions of typhoid fever.* The five other unvaccinated chickens are more or less ill, one seriously so. As to the twelve vaccinated chickens, not one has died, and to-day† they are all alive, and in good health. We may now sum up the results as follows:

It is the life of a parasite, in the interior of the body, which causes the disease known as chicken cholera and which causes death by this disease. When the cultivation of this parasite cannot take place in the body of a chicken, the disease does not show itself. The chicken is then in the constitutional condition of animals which chicken cholera cannot attack. Animals, in this condition, may be said to be born vaccinated for this disease, because the fœtal evolution has not placed in their bodies the proper food of the parasite, or because substances, which could serve as such food, have disappeared while they were yet young. We must not wonder that there are constitutions more or less apt to receive inoculations of certain kinds of virus, for, as was announced in my first note, the broth of beer-yeast is entirely incapable of supporting the life of

*The blood is full of parasites, and the interior organs are frequently covered with pus and false membranes, particularly next to the intestinal pockets, through which the germ seems to have penetrated.

†April 26th.

the parasite of chicken cholera, while it is well adapted to the cultivation of a multitude of microscopical germs, notably of the bacteridia of carbuncular disease.

The explanation to which we are led by the facts already mentioned, of the different degrees of constitutional resistance of some animals, as well as of the immunity which chickens acquire by preventive inoculations, must seem a natural one, if we take into consideration, that every cultivation modifies the medium in which it takes place. In the case of ordinary plants, the soil is modified; in the case of parasites, the animals and plants on which they live are also modified. The same thing happens with the liquids in which they live, in the case of ferments and other microscopical germs. The modifications which take place have this character in common, that new cultivations of the same species in these media soon become difficult or impossible. If chicken-broth is used for cultivating the germ of *chicken cholera*, and if, after three or four days, the liquid is filtered, to separate all the germs, and furthermore, if after this, fresh quantities of the germs are placed in the filtered liquid, it will be found incapable of producing the feeblest development. Perfectly limpid at first, the liquid remains indefinitely limpid.

We are lead to believe that the cultivation of the attenuated virus in a chicken, places its body in the same state as that of a liquid which can no longer sustain the life of the germ of disease. We may extend the comparison still further, for, if we filter the broth on the second day of the cultivation, instead of on the fourth, the filtered liquid will still permit the cultivation of the germ, but less readily than at first. This may enable us to understand that the cultivation of the attenuated germ in the body of a chicken may not have removed all the food for the germ. The remainder may allow a fresh cultivation of a feebler kind. This is the same as a first *vaccination*. Subsequent inoculations will remove progressively all the materials for the cultivation of the parasite. Through the action of the circulation, a time will come when any new cultivation on the animal will remain unproductive. Then the disease cannot recidivate, and the subject becomes perfectly vaccinated.

It may seem astonishing that the first cultivation could have stopped before all the food of the germ has been destroyed; but we must not forget that the germ is aerobian,* and that, in the body of an animal, it does not find the same conditions as in an artificial

* Pasteur divides germs and other microscopic organisms into *aerobians* (requiring air to live) and *anaerobiae* (which do not require air). — *Translator.*

medium of cultivation, in which there are no obstacles to its propagation. In the body, on the contrary, it finds opposition from the cells of the organs, which are also aerobian, and are continually absorbing oxygen.

We might also account for the fact of non-recidivation by admitting that the life of the germ, instead of destroying certain substances in the body of an animal, on the contrary, adds other substances which act as an obstacle to its further development. The history of the life of these inferior beings, of all beings in fact, authorizes this supposition. The excretions due to vital functions often prevent vital functions of the same nature. In some fermentations, antiseptic products are formed while fermentation is going on, and even by the action of ferments, and these products put an end to further action, even if there are still substances left capable of undergoing fermentation. In the cultivation of our germ, there might, in the same way, be substances formed whose presence might explain non-recidivation and vaccination.

Our artificial cultivation of the parasite will enable us to examine this hypothesis. If we prepare an artificial cultivation of the germ of chicken cholera, we may evaporate the liquid in vacuo while cold, then bring it back to its original volume by the addition of chicken broth. If the extract contains a poison which destroys the germ, and if the presence of this poison is the cause of its non-development, the cultivation of the germ cannot take place in this liquid. On the contrary, the development does take place without difficulty. We cannot then believe that, during the life of the parasite, there are substances produced which prevent its further development. This is a corroboration of the opinion which we have expressed on the cause of non-recidivation in certain virulent diseases.

Abstracts from American and Foreign Journals.

American Chemical Journal.

Abstractor, J. P. BATTERSHALL, Ph.D.

A Method for the Proximate Analysis of Plants, HENRY B. PARSONS (I, 377).—Will be noticed elsewhere.

On the Estimation of Phosphoric Acid as Magnesic Pyrophosphate, F. A. GOOCH (I, 391).—See this JOURNAL (I, 537).

Laboratory Notes, ARTHUR MICHAEL (I, 413).

On monoethylphthalate (I, 413).—This compound was prepared by heating equal parts of absolute alcohol and phthalic anhydride in a flask connected with an upright condenser, for ten hours at 100°, evaporating the excess of alcohol at a low temperature, dissolving the remaining residue in water, and neutralizing it in the cold with barium carbonate. In this way the barium salts of monoethylphthalate and phthalic acid are formed, which can be separated by means of their different solubility in water, the phthalate being much the less soluble. Barium monoethylphthalate forms long, concentrically grouped needles, which are very soluble in water, and possesses the formula,

$$\left(C_6H_4\begin{matrix}COOC_2H_5\\COO\end{matrix}\right)_2Ba.$$

The corresponding silver salt is prepared by precipitating a concentrated aqueous solution of the barium salt with silver nitrate; it forms beautiful long needles, which blacken on exposure to the light. The free monoethylphthalate, which was obtained by treating a solution of the barium salt with the calculated quantity of sulphuric acid and evaporating the filtrate in vacuo, is a heavy oil, remarkably unstable when heated, even upon a water-bath. With a view of obtaining the chloride, $C_6H_4\begin{matrix}COOC_2H_5\\COCl\end{matrix}$, equivalent amounts of monoethylphthalate and phosphorus trichloride were heated in a retort over a water-bath. The results of this reaction were the evolution of chlorhydric acid and ethyl chloride and the formation of a heavy oil, which proved to be diethylphthalate, $C_6H_4(COOC_2H_5)_2$, showing that the chloride of monoethylphthalate, first formed, undergoes a condensation, and is decomposed into phthalic anhydride and ethyl chloride, the formation of diethylphthalate being probably due to a portion of the ethyl chloride reacting on unchanged monoethylphthalate.

On a new formation of ethyl mustard oil (**1**, 416).—A mixture of ethyl iodide and mercuric sulphocyanate was heated in a tube for about two hours, at 145°, and the resulting compounds brought into a flask connected with a condenser, and treated with steam as long as an oil distilled over. This oil was separated, dried over $CaCl_2$, and distilled at 135°. It possessed the odor of ethyl mustard oil, and, when mixed with aniline, gave a precipitate which, when purified by crystallization from water, possessed the properties of phenylethylsulphocarbamide. The amount of ethylsulphocyanate formed in the above reaction greatly exceeds that of the ethyl mustard oil. Both compounds, however, are produced in very small quantities, the principal product of the reaction being a red mass, previously mentioned by Schlagenhauffen,* and probably consisting of a double compound of ethyl mustard oil with mercuric iodide.

On the preparation of methyl aldehyde (**1**, 418).—Monochlormethyl acetate is first prepared by passing a current of dry chlorine gas through methyl acetate for about seven hours, the liquid being placed in a flask surrounded by cold water. On submitting the contents of the flask to fractional distillation, and separating the portion which passes over between 100–120°, a very satisfactory yield of monochlormethyl acetate is obtained. This, when mixed with water and placed in a strong closed flask, and heated for about an hour at 100°, furnishes an abundant supply of methyl aldehyde, which is separated by exactly neutralizing the contents of the flask with sodium hydrate, and distilling. The above reaction is expressed by the equation:

$$CH_2\begin{matrix}Cl\\ O\end{matrix} - OC - CH_3 + H_2 = CH_2O + O + C_2H_4O_2 + HCl.$$

On the "migration of atoms in the molecule," and Reimer's chloroform aldehyde reaction (**1**, 420).—This article is wholly speculative in character and, not forming a record of personal investigation, possesses only a theoretical interest.

On the Oxidation of Substitution Products of Aromatic Hydrocarbons, IRA REMSEN and C. FAHLBERG (**1**, 426).

On the Oxidation of Orthotoluenesulphamide.

Preparation of orthotoluenesulphamide (**1**, 426).—The sulphonic acids formed by treating toluene with fuming sulphuric acid, were converted by aid of the usual reactions into the corresponding chlorides, from which the liquid orthotoluenesulphochloride was

* Ann. Chem. Phys. (3), **56**, 297.

isolated. This, upon treatment with ammonia, was converted into orthotoluenesulphamide, which melts at 153–154° and, by fusion with potassium hydroxide, yields salicylic acid.

Formation of benzoic sulphinide.—The amide thus obtained was heated for ten hours on a water-bath, together with potassic permaganate, the excess of permanganate reduced by adding alcohol, the solution filtered, and hydrochloric acid added to the concentrated filtrate. The precipitate formed, gave, on analysis, figures corresponding to the formula, $C_7H_5O_3NS$, which differs from the normal sulphamine acid produced from the corresponding para compound, in that it contains a molecule of water less. This body may be regarded as a condensation product, having the formula,

$$C_6H_4\begin{cases}CO-\\SO_2NH\end{cases}$$

The authors note that a similar grouping of a carboxyl and an amido group, is a characteristic feature of some compounds allied to indigo, such as isatine, and suggest, as a proper designation of such compounds, the term *sulphinides.* Benzoic sulphinide (or anhydrosulphaminebenzoic acid) crystallizes in short prismatic forms, which fuse at 220°. It is difficultly soluble in cold water, but dissolves readily in alcohol and in ether. *It possesses a marked sweet taste, being much sweeter than cane sugar.* By fusion with potassium hydroxide, benzoic sulphinide is easily and completely converted into salicylic acid. By neutralizing its aqueous solution with various carbonates, the corresponding salts were obtained. In this manner the barium, magnesium, lead, potassium and ammonium compounds were prepared.

Orthosulphobenzoic acid.—On further evaporating the filtrate obtained in the preparation of benzoic sulphinide, a crystalline potassium salt separates out, which is purified from the accompanying potassium chloride by recrystallization. The analysis gave figures corresponding to monopotassiumsulphobenzoate, $C_6H_4\begin{cases}SO_3K\\CO_2H\end{cases}$

This compound belongs to the ortho series, as is shown by the formation of salicylic acid when it is fused with potassium hydroxide. It is precipitated from concentrated solutions by addition of hydrochloric acid and, upon recrystallization, forms beautiful, large rhombic plates. Benzoic sulphinide and orthosulphobenzoic acid are formed in about equal quantities by the oxidation of orthotoluenesulphamide, *i. e.*, from two molecules of the latter one molecule of each of the former compounds is obtained. Orthosulphobenzoic acid, $C_6H_4\begin{cases}CO_2H\\SO_2H\end{cases}$ crystallizes in fine large plates, which fuse at 240°,

undergoing decomposition; it is easily soluble in water, but scarcely dissolves in alcohol or in ether.

Acid barium orthosulphobenzoate crystallizes in needles, which suffer partial decomposition at 250°. Orthosulphobenzoic acid can be prepared from benzoic sulphinide by heating this compound in a sealed tube to 150°, with concentrated hydrochloric acid. In a reverse manner, when the neutral potassium salt of orthosulphobenzoic acid is treated with phosphorus pentachloride, the product treated with ammonia, and hydrochloric acid is added, a precipitation of benzoic sulphinide occurs. Phthalic acid, when submitted to the above treatment, yields an imide of the formula, $C_6H_4\begin{matrix}CO\\CO\end{matrix}>NH$, differing, however, in properties from Laurent's phthalimide. The authors further mention an unsuccessful attempt to convert orthosulphobenzoic acid into phthalic acid, by treatment with sodium formate.

On an Unusual Case of Electrolysis, J. W. MALLET(1, 438).—The author notes that a Smee's galvanic battery, not being in use, was laid aside, when the plates, which were originally raised out of the acid, accidently became immersed in the liquid, which was of unusual strength. It was afterwards found that the zinc plates were very much corroded, and that one of the sheets of platinized silver foil was thickly coated with zinc, of which over 30 grms were removed. The battery liquid had doubtless first become converted into zinc sulphate, which had subsequently acted as a "decomposing cell," and metallic zinc was electrolytically deposited from its salt.

Berichte der Deutschen Chemischen Gesellschaft.

Abstractor, ARNO BEHR, Ph.D.

On Methylated Diethyleneamines, H. F. MORLEY (13, 222).—Monomethyldioxethyleneamine and dimethyloxethyleneamine were prepared by the action of chlorhydrine ($C_2H_4Cl.OH$), on methylamine and dimethylamine respectively.

On the Oxidation of Substituted Phenols, G. MAGATTI (13, 224).—The acetylated compound of tetrabromparadiphenol, dissolved in glacial acetic acid, is oxidized by fuming nitric acid. The result is a crystalline body of the formula of tetrabromdiphenylquinone, $C_6H_2.C_6H_2.Br_4O_2$. This is a simple analogue to cedriret, a colored substance found in wood-tar.

On Some Derivatives of Parabromaniline, M. DENNSTEDT (**13**, 228).—A number of these derivatives, such as bromphenylurethane, bromphenylcyanate, bromphenylglycocol, etc., were prepared according to the usual methods.

Crystallographic Description of Benzylorthothioformic Ether, $CH(C_7H_7S)_3$, M. DENNSTEDT (**13**, 238).

Discussion of the Question if Hypoxanthine is a Product of the Decomposition of Certain Albuminoids, E. DRECHSEL (**13**, 239).—Not suitable for abstraction.

On Dinitroparatoluidine, F. BEILSTEIN (**13**, 242).—This paper treats on the molecular constitution of two isomeric dinitroparatoluidines, one prepared by Beilstein and Kuhlberg, by nitration of paraacettoluide, and the other prepared by Tiemann, by reduction of trinitrotoluole.

On Ethylene Iodopicrate, L. W. ANDREWS (**13**, 244). — This substance, of the formula $C_6H_2(NO_2)_3O.C_2H_4I$, was prepared by acting on silver picrate with a solution of ethylene iodide in chloroform.

On a New Class of Ammonium Compounds, PETER GRIESS (**13**, 246).—This new class of bases is obtained from the isomeric amidophenols with methyl iodide. Orthotrimethylphenolammonium is prepared by adding a concentrated solution of caustic potassa to a mixture of orthoamidophenol chloride and methyl iodide dissolved in methylic alcohol. The orthotrimethylphenolammonium iodide, which is the primary product of this reaction, is decomposed by argentic oxide. On evaporation, the watery solution yields crystals of the hydrate of the new base. The anhydrous base is obtained by heating to 105° C. Its composition is represented by the formula:

$$C_9H_{13}NO = C_6H_4 \begin{cases} O \\ | \\ N(CH_3)_3 \end{cases}$$

By dry distillation, the free base is transformed into an isomeric substance, which was obtained in the form of an oil, and proved to be orthodimethylamidoanisole: $C_6H_4 \begin{cases} O.CH_3 \\ N(CH_3)_2 \end{cases}$ The chlorohydrate of the base, on heating, yields methyl chloride and orthodimethylamidophenol: $C_6H_4 \begin{cases} OH \\ N(CH_3)_2 \end{cases}$. Paratrimethylphenolammonium was also prepared from paramidophenol, in an analogous manner, with methyl iodide, but when the latter was replaced by ethyl iodide, a different reaction took place.

On Vesbium and Norwegium, C. RAMMELSBERG (**13**, 250).—The author calls attention to communications regarding these new

elements, made by Scacchi, in the *Transactions of the Academy of Sciences of Naples*, and by Dahll, in the *Zeitschrift der Geologischen Gesellschaft*.

Regarding Albuminoids, A. STUTZER (13, 251).—Preliminary notice, showing that the hydrated oxide of copper can be used for the separation of the albuminoids, proper, from other nitrogenous bodies, such as asparagine, leucine, the alkaloids, etc., which do not form insoluble compounds with it, and showing further, that by the action of pepsine and hydrochloric acid on albuminoids, only a certain proportion of these substances is decomposed in the generally known manner, while on another definite proportion this reagent has no effect. This refractory substance seems to contain phosphorus, and to be related to nucleine.

On Tropidine, A. LADENBURG (13, 252).—The author finds that this substance, first described by him, *Ber. d. d. chem. Gesell.*, 12, 944, can be prepared in a state of greater purity by the action of dilute sulphuric acid on tropine, $C_8H_{15}NO = C_8H_{13}N + H_2O$. The paper contains, also, a crystallographic description of the chloroplatinate of tropidine.

On Hyoscyamine, A. LADENBURG (13, 254).—This paper contains several experiments undertaken to decide the question, if hyoscyamine is identical or isomeric with atropine. Though the products of decomposition of hyoscyamine with barytic hydrate, seem to be identical with those of atropine, the author thinks that the alkaloids themselves are not identical.

On Duboisine, A. LADENBURG (13, 257).—After purification of the base by transformation into the compound of its chloride with gold chloride, which forms a well crystallized body, it was found to be identical with hyoscyamine.

History of the Law of Periodical Atomicity, LOTHAR MEYER (13, 259).—Contains a reclamation of the author's share in the development of the law of periodical atomicity.

On the Acetyl Compounds of some Carbohydrates Prepared according to Liebermann's Process, A. HERZFELD (13, 265).—The author some time ago prepared and described a series of acetyl compounds of carbohydrates, following the above mentioned process. Further investigation has shown that this process—boiling with acetic anhydride and sodium acetate—furnishes, in each case, a compound in which the hydrogen atoms of all the hydroxyl groups contained in the carbohydrates, are replaced by acetyl groups.

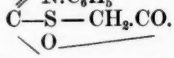
Thus octacetyl diglucose and the octacetyl compounds of galactose, saccharose, maltose, and the triacetyl compounds of erythro- and achroodextrine, were obtained. The number of acetyl groups was ascertained by decomposition with dilute sulphuric acid and titration.

On "Rouge Francais," W. v. MILLER (**13**, 268).—This dyestuff, which is now manufactured in France, and is used for dyeing wool crimson, is a mixture of two coloring substances produced by the action of diazonaphthalenesulpho acid and diazobenzolesulpho acid on betanaphthole. The author found it advantageous to use zinc dust and pure water, without any acid, for the splitting up of these azo compounds.

On Oxacrylic Acid, P. MELIKOFF (**13**, 271).—Monochlorolactic acid, obtained by the addition of hypochlorous acid to acrylic acid, when treated with alcoholic potassa, loses HCl and yields the new substance. It can be obtained in crystals, and forms a number of crystalline salts. If the watery solution of the lime salt is heated to boiling, the latter is transformed into the lime salt of glycerinic acid. By heating with water, the free acid can also be transformed into glycerinic acid. This transformation consists in the addition of the elements of one molecule of water.

On the New Lines in the Spectrum of Hydrogen, and the Dissociation of Calcium, HERMANN W. VOGEL (**13**, 274).—Not suitable for abstraction.

On Phenyl Mustard Oil Glycolide, C. LIEBERMANN and M. VOELZKOW (**13**, 276).—This new body is prepared by heating phenylsulphurethane, or mustard oil, with chloracetic acid and alcohol, to 160° C. Its composition is represented by the formula,



When decomposed by boiling with a solution of barytic hydrate, it yields carbonic acid, aniline and sulphoglycolic acid.

Contributions to the Knowledge of the Aromatic Products of the Animal Body, E. BAUMANN (**13**, 279).—The author had found that hydroparacumaric acid was the principal product of the putrefaction of tyrosene. He thought it probable that the same acid might be formed from albuminoids, during the process of digestion in the animal body, and looked for it in human urine. He found an aromatic oxy acid of similar properties, which, however, proved to be the lower homologue of the hydroparacumaric acid, that is, paraoxyphenylacetic acid.

On the Action of Phosphorus Pentachloride and Phosphorus Oxychloride on Cinchonine Chloride, W. KOENIGS (**13**, 285).—Phosphorus pentachloride and phosphorus oxychloride do not react singly with cinchonine, but a mixture of both does. A new derivative of cinchonine, containing chlorine, is produced. Its formula is either $C_{19}H_{21}ClN_2$ or $C_{19}H_{19}ClN_2$.

On the Production of Anthranilic Acid from Orthonitrotoluole, PH. GREIFF (**13**, 288).—A substance of the empirical formula of a bibromnitrotoluole, had been prepared by Wachendorff from orthonitrotoluole and bromine. But, being soluble in alkalies, its constitution might be expected to be different from that of bodies of the class mentioned. The author finds that it is, in fact, bibromanthranilic acid, and calls attention to the remarkable reaction by which oxygen and hydrogen, contained in the nitro and methyl groups, change their places within the molecule during the reaction with bromine. $C_6H_2Br_2.NO_2.CH_3$, bibromnitrotoluole. $C_6H_2Br_2.NH_2.CO_2H$, bibromanthranilic acid.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office**, by ARNO BEHR.

May 4, 1880.

227,168.—*Insulating compound for telegraph wires.* WILLIAM W. JACQUES.

Bees-wax and Venice turpentine.

227,268.—*Coating iron surfaces.* JOSEPH KINTZ.

Claim: The process for bronzing iron surfaces, which consists in cleaning and buffing the iron surfaces, then electroplating with copper, then dipping in acid solution, then again buffing, then boiling in a salt-of-tin solution, and then finishing by subjecting the article to heat, until the copper and spelter coatings are fused into bronze.

May 11, 1880.

227,352.—*Composition for insulating telegraph wires, coating metals, covering roofs, and for other purposes.* EDGAR EVERHART.

Consists of resin or lac, asphalt, coal-tar or pitch, powdered charcoal and infusorial earth.

227,395.—*Triturating and mixing apparatus.* JAS. TREGURTHA.

227,396.—*Dissolving apparatus.* JAS. TREGURTHA.

227,448.—*Galvanic Battery.* ROBERT SCHLUMBERGER.

227,463. *Preparation of paper stock from colored rags.* GEORGE F. WILSON and PHILIP O'REILLY.

Claim 4 : The process of preparing colored rags for paper pulp, by boiling the stock with alkali to remove oil and grease, washing, treating it with a salt of manganese and then with chloride of lime, washing and subjecting it to the action of oxalic acid.

227,464.—*Manufacture of wood pulp for paper.* GEORGE F. WILSON and PHILIP O'REILLY.

Claim 3 : The process of making pulp from the Yucca or other wood, by inducing fermentation in the pores of the wood, washing, treating with alkali, washing and bleaching.

227,470.—*Manufacture of artificial indigo.* ADOLF BAEYER.

This patent contains the latest discoveries of A. Baeyer with regard to the artificial production of indigo. He found that several derivatives of orthonitrocinnamic acid can be, by smooth reactions, transformed into indigo. Orthonitrobromhydrocinnamic acid, boiled with alcoholic potassa, yields orthonitrophenylpropiolic acid, $C_6H_4NO_2.C{\equiv}C{-}CO_2H$. A solution of the latter, in an excess of alkali, boiled with a reducing agent like glucose, or milk sugar, yields indigo in a crystalline form.

Another derivative of orthonitrocinnamic acid, orthonitrophenyloxacrylic acid, can be converted into indigo blue by the mere action of heat.

227,480.—*Method of preparing absorbent cotton.* LUCINDA A. BUCKNAM.

This method consists in a preparatory treatment of the cotton with a solution of chloride of lime and a solution of caustic soda, for its preparation as an absorbent for surgical purposes.

227,559.—*Safety paper and method of preparing the same.* JAMES H. MCMAHON.

Treating the paper with an alcoholic solution of tannin.

227,561.—*Manufacture of bicarbonate of soda.* WILLIAM T. MENZIES.

A process for the purification from, and removal of, the ammonia and organic coloring matter existing in bicarbonate of soda manufactured by the ammonia process, which consists in passing a current of carbonic acid through dry bicarbonate of soda while under heat and pressure.

227,564.—*Apparatus for manufacturing vinegar.* VICTOR MICHAELIS.

227,588.—*Manufacture of anthracene.* FRITZ SALATHÉ.

The patent is based on the fact that petroleum hydrocarbons can be converted into aromatic hydrocarbons, including anthracene, by heat. According to the patent, petroleum is passed through iron retorts filled with charcoal and heated to a dull red. The product is called anthracitic tar, and is claimed to be free from acid matters.

227,601.—*Explosive compound.* ROBERT W. WARREN.

One part of nitro-cellulose is dissolved in ten parts nitro-glycerine in the cold. To this mixture pulverized nitro-cellulose is added until the mass is brought to the consistency of a dry powder. This is further mixed with gunpowder.

May 18, 1880.

227,629.—*Method of producing multiple copies of writings.* EMIL HOLTZMANN.

This patent is for the well known hektograph. The method was patented in Germany, April 30, 1878. Claim 1 describes the process as consisting in causing a surface of glue or gelatine, rendered uniformly moist and absorbent by soaking it in water, to take up the colors from an original drawing or writing, so as to form the desired negative impression, and pressing the damp paper, on which the impression is to be reproduced in a positive form. upon the gelatine thus prepared.

227,676.—*Manufacture of paper pulp from straw.* CHARLES O. and HENRY A. CHAPIN.

The straw is roasted previous to chemical or mechanical treatment.

227,698.—*Apparatus for collecting natural mineral water and charging liquids with natural carbonic acid gas.* ALBERT K. MCMURRAY.

227,801.—*Galvanic battery.* WILLIAM V. LOCKWOOD.

The porous cell contains peroxide of lead and sulphuric acid.

227,849.—*Anti-friction composition for bearings.* JOHN SMALLEY.

Consists of graphite and shellac.

Reissue 9,203.—*Chlorinating ores.* J. HOWELL MEARS.

The ore is treated with chlorine gas under pressure.

May 25, 1880.

227,902.—*Extracting copper from ores.* THOMAS S. HUNT and JAMES DOUGLAS.

The solution of cupric chloride, which is extracted from the ore, is treated with sulphurous acid. Cuprous chloride is precipitated, and the remaining acid solution, containing hydrochloric and sulphuric acids, is utilized in the further extraction of the ore.

227,945.—*Process and apparatus for reducing asphaltum to a liquid.* DAVIS W. BAILEY.

The process consists in melting together crude or refined asphaltum with the residuum of petroleum, or with wax tailings.

227,963.—*Depositing gold from its solutions.*—WILLIAM MORRIS DAVIS.

Solutions of gold filtered through charcoal deposit it in the metallic state.

228,004.—*Process for recovering precious metals from liquids in which they are suspended.* JOHN TUNBRIDGE.

Claim: The process of separating metals from jewelers' waste, mining waters, etc., by treating said waters with soapy solutions and subsequent filtration.

228,005.—*Insulating compound for telegraph wires.* JOHN VAN WINKLE and FELIX DONELLY.

Consists of coal-tar, pitch, tallow and potash.

228,016.—*Compound for preserving meat.* FILIPPO ARTIMINI.

A compound called "boric tartrate," the composition of which is not given in the claim.

228,028.—*Coating the interior of vessels for holding oils.* DANIEL F. BOWKER.

After two coatings with a mixture consisting of glue, molasses, alum, glycerine, potter's clay and water, a solution of bichromate of potash is applied to the surface of the coatings.

228,029.—*Asphalt varnish.* JULIUS BRACE.

A solution of asphaltum in naphtha and some heavier part of petroleum.

228,140.—*Process of obtaining gold from its ores.* ANSON C. TICHENOR.

Claim 2: The process of treating gold ores for the subsequent recovery of the precious metals, said process consisting in subjecting the the said ores to the action of a chloride of gold.

Foreign Patents.

Condensed from R. BIEDERMANN'S Report to the German Chemical Society, by OTTO H. KRAUSE.

H. BUESSING, Braunschweig: *Precipitation of white lead from solutions of basic acetate of lead.* (Germ. P., No. 4505, June 16, 1878.)—Carbonic acid is admitted to a vessel having a conical bottom fitted with pipes for heating the lead solution it contains. A shaft, to the arms of which blades of wicker work are attached, stirs the liquid, and an endless screw conveys the precipitated white lead to the discharge opening.

RAPHAEL MELDOLA, Hackney Wiek.: *Coloring matters from the sulphonic acids of phenols and from diazosulphonic acids derived from amines.* (Engl. P., No. 1864, May 10, 1879.)—The diazosulphonic acids of benzole, naphthalene, &c., are made to react on phenol-, naphthole-, resorcine-, etc., sulphonic acids. Various shades of orange and scarlet dyes are formed. Orange, for instance, by dissolving 10 parts sulphanilic acid in 20 times its weight of water, and treating with 4 parts sodium nitrite and hydrochloric acid. The diazobenzolesulphonic acid produced, is poured into a solution of 19 parts of sodium β-naphtholedisulphonate in 8 times its weight of water. After neutralizing with ammonia, the coloring matter is precipitated with sodium chloride. Scarlet is prepared in a similar manner from xylidinesulphonic acid and β-naphtholesulphonic acid.

H. GUENTHER, Berlin: *Black printing ink and etching ground.* (Germ. P., No. 9566, October 28, 1879.)—Composed of 40 parts pitch or asphaltum, 28 parts rectified terpentine, 8 parts aniline violet, and 24 parts of the residue from the distillation of rosin oil.

F. GRAESSLER, Canstatt: *Preparation of amidoazobenzinesulphonic acid.* (Germ. P , No. 9384, September 28, 1879; addition to Germ. P., No. 4186, May 12, 1878.) (See also this JOURNAL, **1**, 499.)—The inventor claims the use of oil of vitriol for this purpose, and also the employment of sulphuric anhydride and sulphuric chlorhydrate.

HENRY PARKES, Birmingham: *Improvements in the methods of working nitro-cellulose.* (Engl. P., No. 1869, November 10, 1879.)—Nitro-cellulose is made plastic by the addition of different substances: carbon tetrachloride and camphor, equal parts; carbon disulphide and camphor, also the liquid obtained by the action of sulphurous acid upon camphor; finally, solutions of camphor in benzine, gasoline, naphtha, turpentine, paraffine, oil, &c. The softened mass, with or without addition of coloring matters and resins, is pressed in heated moulds. In a second patent (Engl. P., No. 1866, May 10, 1879) he claims the use of nitro-cellulose, softened by means of the above mentioned substances, in combination with shellac and glycerine or castor oil, as a varnish.

ALEX. SCOTT, J. D. SCOTT and T. R. OGILVIE, Greenock: *Purification of sugar solutions.* (Engl. P., No. 1809, November 10, 1879.)—To remove the salts from the sugar solution, the latter is run into a mixture of sulphuric acid and alcohol. Should the liquid, separated from the precipitate, still contain organic impurities, lime is added to alkaline reaction, or a larger amount of lime is added to precipitate saccharate of lime. According to another process, alcohol is added to the sugar solution, and then saccharate of lime precipitated. Neither process is new.

MATTHEW BIRD, London: *Substitute for leather.* (Engl. P., No. 1879, May 13, 1879).—Comminuted leather waste is mixed with vegetable fibres, preferably spent tan bark, talc, asbestos and isinglass added, and the mixture pressed into moulds, or between rollers.

R. M. ATWATER, Melville, and JAMES WHITALL, Philadelphia: *Improvements in glass furnaces, and in the manufacture of glass.* (Germ. P., No. 8387, February 29, 1880.)—The composition is melted at a high temperature, in a separate, rotary furnace. The finished glass *metal* is then run into a working furnace, which is kept at a much lower temperature. The heat passing off, is first utilized in keeping the annealing ovens at the proper heat.

ADOLPH ROSE, Braunschweig: *Manufacture of barium hydrate from barium sulphide.* (Germ. P., No. 9828, June 7, 1878.)—Barium sulphide, reduced from the sulphate, is placed in a suitable apparatus, and extracted with the aid of water and steam, whereby a very concentrated solution results. If this solution, in a less concentrated state, be exposed for some time to a temperature of 50–60° C., barium hydroxide, and a higher sulphide of barium is formed. The barium hydrate crystallizes from the hot solution, and the small quantity of barium sulphide, with which the crystals are contaminated, is removed by a solution of zinc oxide, in baryta water. Solution of the reduced sulphide with steam and water is essential, as, otherwise, barium monosulphide is chiefly extracted, and little barium hydroxide obtained.

T. FLEITMANN, Iserlohn: *Preparation of nickel containing zinc.* (Germ. P., No. 9405, September 6, 1879.)—A mixture of nickel oxide and zinc oxide is reduced. The zinc is incompletely volatilized, about 10 per cent. uniting with the nickel. The mixture of the oxides is obtained either by precipitating a mixed solution of these metals, or by calcining the sulphates, or oxalates, of nickel and zinc.

J. B. SPENCE, London: *Treatment of metallic sulphides.* (Engl. P., No. 2006, May 20, 1879.)—Instead of heating the sulphides to redness, as described in his previous patent, No. 1855, of 1879, treating with sulphuric acid, and again heating (see this JOURNAL, **2**, 193), the inventor now omits the calcination, and boils the very finely pulverized ores with sulphuric acid. Hydrogen sulphide is evolved, if dilute acid be employed; sulphurous acid is obtained, if concentrated acid be used. The sulphates thus obtained from ores mainly composed of lead and zinc sulphides, are finely pulverized, and used as pigments.

GEBRUEDER RAMDOHR, Wansleben: *Basic lining for furnaces.* (Germ. P., August 19, 1879.)—Bricks made of magnesium chloride, clay and iron ore, are calcined in the oxidizing flame, or in presence of superheated steam, whereby magnesia is produced. The inventors make use of this (long known) reaction, to produce a highly magnesian material, for lining furnaces.

ROMAIN JOLY, Elboeuf: *Carbonisation of vegetable fibres, &c., contained in woolen fabrics.* (Germ. P., No. 9263, February 12, 1879.)—Claims the use of the chlorides of aluminium, zinc and magnesium, for this purpose. (These substances have all been employed before with the same object. See Wagner's Jahresber., 1878, 1024; also, as regards magnesium chloride, A. Frank, Germ. P., No. 2301.)

JUL. ATHENSTAEDT, Bad Essen: *Method of preparing acetotartrate of alumina as an antiseptic.* (Germ. P., No. 9790, November 24, 1879.)—This compound acts as a mild astringent. It can be obtained as a dry powder, or as a gummy mass, by dissolving basic acetate of alumina in tartaric acid, or by mixing a solution of acetate of alumina with tartaric acid, and evaporating. Its quantitative composition is not constant.

VICTOR VON OFENHEIM, Vienna: *Method of bleaching ceresine, paraffine, petroleum, stearine, and other fatty matters, by means of the hydroxides of aluminium, iron, manganese and magnesium.* (Germ. P., No. 9291, August 21, 1879.)—Ozokerite is heated to 170–200° C., and about 20 per cent. of the above mentioned substances added to the molten mass. This treatment is repeated several times, with the clear liquid which separates upon standing. The residues are treated with steam to remove ceresine, and to restore the hydroxides.

L. DANKWERTH and F. SANDERS, St. Petersburgh: *Artificial caoutchouc.* (Germ. P., No. 9620, June 18, 1879.)—Composed of equal parts by weight of wood-tar oil, coal-tar oil, hemp oil and linseed oil, to which are added small quantities of ozokerite, spermaceti and sulphur.

WILLIAM GARTON, Southampton: *Improvements in the manufacture of starch, and recovery of the ammonia employed.* See this JOURNAL, **2**, 105.

F. W. MARQUARDT, Hanover: *Preparation of yeast.* (Germ. P., No. 9534, September 19, 1879.)—The albuminoids of malt germs are converted into peptones, by means of acidified glucose, or syrup, or acidified water only. The extracted peptones are used in making compressed yeast.

SPORMANN, Hamburg: *Treatment of rancid butter.* (Germ. P., No. 9483, October 2, 1879.)—The butter is kneaded with lime-water.

THE AMERICAN CHEMICAL SOCIETY.

XXVII.—Proceedings.

Regular Meeting held June 3rd, 1880.

The meeting was called to order at 8 P.M. Dr. A. R. Leeds in the chair.

In th absence of a quorum at that hour the regular business of the Society was deferred.

Mr. Jas. H. Stebbins, Jr., B.S., read a paper, on "Some New Coloring Matters Produced by the Action of Diazo Compounds on Phenols."

At the conclusion of the paper Dr. Geyer asked how amido-betanaphthol was recognized.

Mr. Stebbins replied that he recognized this body by its analysis.

Dr. Behr asked how Mr. Stebbins knew when the splitting up of the compounds under the influence of reducing agents, was finished, so that the nitro groups should not also be reduced.

Mr. Stebbins promised further details on this point next fall.

Dr. Behr remarked that amidopyrogallol appeared to be a new body, and deserved a longer description.

Mr. Stebbins promised to describe this body more fully in another paper.

Dr. Bourgougnon asked if the new colors were "faster" than aniline colors.

Mr. Stebbins said that many of them were much faster.

Dr. Behr remarked that one of these azo colors was called "fast red," because of its "fast" qualities.

There now being a quorum, the meeting took up the regular business of the Society.

The minutes of the meetings held April 1st and May 6th, 1880, were read and approved.

The Chairman then called for the reading of the report of the Treasurer.

Before the report was read, Mr. W. H. NICHOLS, the Treasurer, remarked that there was a lack of promptness on the part of members in handing in dues. He said he had put a note on his calls for dues, that members "remit promptly;" but this did not bring about the desired result. He also remarked that if the dues were paid, they would be sufficient to meet all the demands upon the treasury of the Society.

The report of the Treasurer was then read and approved.

The Chairman appointed Messrs. S. A. GOLDSCHMIDT and JAS. H. STEBBINS, as tellers to count the votes in the election of Messrs. ALEXANDER COCHRANE, HUGH COCHRANE and LUCIUS PITKIN, as associate members of the Society. Dr. GOLDSCHMIDT reported each of these gentlemen unanimously elected.

The resignations of Mr. CHARLES DE LAMOTHE and Dr. H. VON GEHREN were voted on and accepted.

The nomination papers of the following gentlemen were then read:

Mr. HERMANN POOLE, Practical School, Buffalo, N. Y.; nominated as a member by E. WALLER, ALBERT H. CHESTER and J. B. HERRESHOFF.

Dr. KARL STAHL, Tacony Chemical Works, Philadelphia; nominated as a member by BRUNO TERNE, ARNO BEHR and O. H. KRAUSE.

G. T. BIHN, 523 Tasker Street, Philadelphia; nominated as a member by BRUNO TERNE, ARNO BEHR and O. H. KRAUSE.

C. H. TORRY, School of Mines, Columbia College; nominated as a member by A. H. ELLIOTT, W. H. NICHOLS and E. WALLER.

THOMAS HARRISON, Philadelphia; nominated as an associate member by W. H. NICHOLS, ALBERT R. LEEDS and A. H. ELLIOTT.

J. R. SAVAGE, Philadelphia; nominated as an associate member by W. H. NICHOLS, ALBERT R. LEEDS and A. H. ELLIOTT.

The Recording Secretary then read a letter from CHARLES MCINTIRE, Jr., telling of the death by drowning of his brother, HENRY MCINTIRE, at Carondelet, on the Mississippi, on April 26th. HENRY MCINTIRE was elected a member of the Society on January 2nd, 1879.

Dr. GOLDSCHMIDT then moved that a committee of five members be appointed to arrange for some meeting of the Society,

either formal or informal, in Boston, during the session of the American Association for the Advancement of Science.

This motion was carried with one dissenting vote.

After some discussion it was proposed that the First Vice-President should appoint this committee. The motion, being put to vote, was carried unanimously.

The meeting then discussed the advisability of taking action at that time upon a proposition of the editors of the *Sanitary Engineer* to form a Sanitary Section of the Society. It was resolved that the matter be deferred until the September meeting of the Society.

After which Dr. E. R. SQUIBB took the Chair, and the following papers were read by Dr. A. R. LEEDS:

1. "On the Action of Light and Darkness on Standard Ammonium Chloride and Tannin Solutions."

2. "On the Action of Light on the Soluble Iodides, with the Outlines of a new Method in Actinometry."

3. "On the Laws Governing the Decomposition of Equivalent Solutions of Iodides, under the Influence of Actinism."

4. "On the Action of Hyponitric Anhydride on Organic Bodies."

After which the meeting adjourned.

ARTHUR H. ELLIOTT,
Recording Secretary.

XXVIII.—On Some New Coloring Matters, Produced by the Action of Diazo-Compounds on Phenols.

By Jas. H. Stebbins, Jr., B.S.

The study of the action of diazo-compounds on phenols dates back a good many years, but it is only within the last few years that it has met with any practical success, and I will now take the opportunity to give a brief sketch of some of the most interesting and valuable compounds, before entering on the description of my own results.

In 1875, P. Gries made the discovery that diazobenzolesulpho acid (from sulphanilic acid), acting on phenols, produced a series of inter esting compounds, which were characterized by more or less tinctorial power.

In the spring of the following year, he sent a communication to the German Chemical Society,* describing this reaction. The great tinctorial power of these new compounds lead him to believe that they might be used with advantage in dyeing and printing, and several samples sent to an expert on colors, proved that his theory was correct, as may now be seen by the great demand for Poirrier's oranges, Nos. 1 and 2, chrysoine, tropaeoline, aecht-roth, roccelline, etc. Among this group the following compounds† deserve special attention, viz :

Parazosulphoxylbenzolephenol, $C_6H_4(\overset{4}{HSO_3}) - \overset{1}{N} = \overset{1}{N} - C_6H_4\overset{4}{OH}$.

This is prepared by the action of diazosulphanilic acid on an alkaline solution of phenol, these two being taken in equal molecules. The yellow-red liquid thus produced, is allowed to rest for a short time, then heated to boiling, and saturated with acetic acid. On cooling, a large number of little yellow leaflets crystallize out, and constitute the acid potassium salt. These are then collected on a filter, dissolved in water, and purified by boiling a short time with a little animal black.

The free acid may be obtained by treating a hot and concentrated solution of the acid potash salt with a large excess of strong hydrochloric acid. It is purified by washing with dilute HCl, and finally crystallized from an acidified aqueous solution. It crystallizes from its concentrated aqueous solution in yellow-red prisms, with a strong violet lustre. It is pretty soluble in alcohol, but nearly insoluble in ether or hydrochloric acid.

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* Ber. d. d. chem. Gesell., 9, 627.

† Ber. d. d. chem. Gesell., 11, 2192.

Nitric acid, even diluted with 3–4 times its bulk of water, decomposes it, with formation of yellow, oily drops, which, after a while, crystallize. This acid has the property of forming acid and neutral salts, with bases.

The acid potassium salt, $C_{12}H_9N_2SO_4K$, may be prepared, besides the already mentioned method, by treating a hot solution of the acid with chloride of potassium.

The following compounds are prepared in exactly the same manner as the previous one, and in their description I will only call your attention to some of the more particular differences.

Metazosulphoxylbenzolephenol, $C_6H_4(\overset{3}{H}SO_3)-\overset{1}{N}=\overset{1}{N}-C_6H_4(\overset{4}{O}H)$. This is prepared by the action of metadiazobenzolesulpho acid on an alkaline solution of phenol. It is easily soluble in water and alcohol, but insoluble in ether.

Azobenzolesulphoxylphenol, $C_6H_5-N=\overset{1}{N}-C_6H_3(\overset{3}{H}SO_3)(\overset{4}{O}H)$, prepared by the action of diazobenzole nitrate on an alkaline solution of orthophenolsulpho acid. The free acid is easily soluble in water and alcohol, but nearly insoluble in ether.

Parazosulphoxylbenzoleorthonitrophenol, $C_6H_4(\overset{4}{H}SO_3)-\overset{1}{N}=N-C_6H_3(\overset{2}{N}O_2)(\overset{4}{O}H)$, prepared by the action of paradiazobenzolesulpho acid on orthonitrophenol; crystallizes from alcohol in pretty, yellow needles.

Parazosulphoxylbenzoleresorcine, $C_6H_4(\overset{4}{H}SO_3)-\overset{1}{N}=N-C_6H_3(OH)_2$, prepared from paradiazobenzolesulpho acid and an alkaline solution of resorcine. The free acid crystallizes in pointed leaflets.

Metazosulphoxylbenzoleresorcine, $C_6H_4(\overset{3}{H}SO_3)-\overset{1}{N}=N-C_6H_3(OH)_2$, prepared in the same way as the previous compound.

Parazosulphoxylbenzoleorcine, $C_6H_4(\overset{4}{H}SO_3)-\overset{1}{N}=N-C_7H_5(OH)_2$, crystallizes in small yellow-red needles.

Parazosulphoxylbenzolesalicylic acid, $C_6H_4(\overset{4}{H}SO_3)-\overset{1}{N}=N-C_6H_3(\overset{2}{O}H)(\overset{1}{C}OOH)$, pretty, yellow needles, soluble in alcohol.

I should like to call your attention here, to the fact, that this is the compound I mentioned in my last paper and which is so similar to the body I described as azobenzoleoxycarboxylbenzole (JOURNAL AMERICAN CHEMICAL SOCIETY, **I**, 466).

Azosulphoxylxyloleresorcine, $C_8H_8(HSO_3)-N=N-C_6H_3(OH)_2$, pretty, yellow-red needles, soluble in alcohol.

Metazosulphoxylbenzole-α-naphthol, $C_6H_4(\overset{3}{HSO_3}) - \overset{1}{N} = N - \alpha\text{-}C_{10}H_6OH$, dark green leaflets, with a golden green lustre, pretty soluble in warm water.

Metazosulphoxylbenzole-β-naphthol, $C_6H_4(\overset{3}{HSO_3}) - \overset{1}{N} = N - \beta\text{-}C_{10}H_6OH$, similar to the previous compound.

Azobenzole-β-sulphoxylnaphthol, $C_6H_5 - N = N - \beta\text{-}C_{10}H_5(HSO_3).(OH)$, prepared by the action of diazobenzole nitrate on an alkaline solution of β-naphtholsulpho acid; red-brown needles, difficultly soluble in water. Besides the three last mentioned naphthol dyes, there are three more similar ones, two being discovered by Poirrier, of Paris, and known as:

Orange No. 1, $C_6H_4(\overset{4}{HSO_3}) - \overset{1}{N} = N - \alpha\text{-}C_{10}H_6(OH)$.

Orange No. 2, $C_6H_4(\overset{4}{HSO_3}) - \overset{1}{N} = N - \beta\text{-}C_{10}H_6(OH)$, and thirdly, one discovered by A. W. Hofmann, of the following composition: $C_6H_5 - N = N - \alpha\text{-}C_{10}H_5(HSO_3)(OH)$, and prepared by the action of diazobenzole, on alphanaphtholsulpho acid.

Parazosulphoxylbenzole-β-naphtholsulpho acid, $C_6H_4(\overset{4}{HSO_3}) - \overset{1}{N} = N - \beta\text{-}C_{10}H_5(HSO_3)(OH)$, acid barium salt crystallizes in deep orange-red microscopic needles.

Azonaphthalenesulphoxyl-β-naphthol, $C_{10}H_6(HSO_3) - N = N - \beta\text{-}C_{10}H_6OH$. This pretty, red dye was first discovered by Caro, and is prepared by the action of diazonaphthionic acid on β-naphthol. I should here like to remark that Poirier claims to have discovered the same dye, which he calls roccelline, and that a controversy is now going on as to the priority of the invention.

Azosulphobenzoic acid—α-oxynaphthoic acid, $C_6H_3(HSO_3).COOH - N = N - \alpha\text{-}C_{10}H_5(OH)(COOH)$, microscopic needles of a brown color.

Azodibromsulphoxylbenzoledioxynaphthalene, $C_6H_2Br_2(HSO_3) - N = N - C_{10}H_5(OH)_2$, violet-brown microscopic needles, soluble in water with a yellow color.

Besides the compounds I have just described, Griess. has discovered quite a number of others, several of which he has patented. Among the prettiest of these may be mentioned anisole red and crimson.

Anisole red is prepared by the action of diazoanisole hydrochlorate on an alkaline solution of β-naphtholsulpho acid. The coloring matter, so obtained, is thrown upon a filter, washed, and dissolved in

water, from which it is reprecipitated with NaCl, in the form of a soda salt. This is very soluble in hot and cold water, and in an acid bath dyes animal fibre of a beautiful red.

Anisole crimson is prepared in the same manner as the foregoing compound, with the exception that β-naphtholdisulpho acid is used, instead of the monosulpho acid.

From what I have described, you will clearly see how neatly diazo compounds react upon phenols, and it will therefore not be necessary for me to give you any more illustrations; and, with your permission, I will now describe a few compounds belonging to this group, and which are, perhaps, not quite as pretty as some of Griess', yet still are interesting enough to deserve your attention.

In my last paper, on the azo colors, I mentioned several bodies, which I will now briefly review, and add certain facts which I at first omitted.

Azobenzoletrinitroxybenzole, $C_6H_5 - N = N - C_6H(NO_2)_3OH$. This was prepared by the action of diazobenzole nitrate on an alcoholic solution of picric acid, taking equal molecules of each. The mixture, thus obtained, soon became filled with long, brown needles. These were thrown upon a filter, washed, and dried under the air pump. This compound is quite explosive, and the melting point could not be obtained on this account. It is soluble in alcohol, with a yellow color, but, on being boiled, it is decomposed, leaving a tarry mass behind. If this compound be treated with reducing agents (as tin and HCl), it should yield aniline and amidotrinitrophenol, according to the following equation:

$$C_6H_5 - N = N - C_6H(NO_2)_3.OH + 2H_2 = C_6H_5NH_2 + C_6H(NH_2)(NO_2)_3OH.$$

But, owing to the great difficulty of obtaining pure reduction products, I have not been able to verify this subject.

Several tests made to obtain this compound by the usual methods, namely, by treating diazobenzole nitrate (prepared by Victor Meyer's method), with an alkaline solution of picrate of potash, have remained fruitless, for the two compounds will not combine, and picric acid was regenerated in each instance. Therefore, it would seem that potash must interfere with their combining, and that the above named compounds can only be formed by treating pure diazobenzole nitrate with an alcoholic solution of picric acid.

Azobenzolepyrogallol, $C_6H_5 - N = N - C_6H_2(OH)_3$. This was obtained by allowing equal molecules of diazobenzole nitrate and an

alkaline solution of pyrogallol to react on one another. Immediately a brick red precipitate is formed, which increases on standing. It was then collected on a filter, washed with water, afterwards with alcohol, and then dried. It dissolves readily in nitrobenzole and glacial acetic acid, at a gentle heat, and crystallizes from them in small, dark red-brown needles. It likewise dissolves slightly in alcohol, and in this shape it is best adapted for dyeing.

Treated with tin and hydrochloric acid, it yields aniline and amidotrioxybenzole.

The positions held by the OH groups in this compound are respectively 1 : 2 : 4.

Parazosulphoxylbenzolephloroglucine, $C_6H_4(\overset{4}{H}SO_3) - \overset{1}{N} = N - C_6H_2(OH)_3$. If equal molecules of diazosulphanilic acid and phloroglucine are allowed to react on one another, the result is a heavy orange colored precipitate, which is collected on a filter, dissolved in boiling water, and precipitated with common salt, in the form of a soda salt. The soda salt is crystallized several times from hot water, and is then in a pretty pure state.

Soda salt, $C_6H_4(\overset{4}{N}aSO_3) - \overset{1}{N} = N - C_6H_2(OH)_3$, fine orange crystalline powder, easily soluble in water. The free acid may be obtained from this by treating the concentrated aqueous solution with an excess of strong hydrochloric acid.

Free acid, $C_6H_4(\overset{4}{H}SO_3) - \overset{1}{N} = N - C_6H_2(OH)_3$. Thin orange colored tables or leaflets, with a strong beetle green lustre. Pretty soluble in water.

Acid barium salt, $(C_{12}H_9N_2SO_6)Ba$, obtained by treating a concentrated aqueous solution of the free acid with a strong solution of baric chloride. Orange colored leaflets, less soluble in water than the soda salt.

If we look back a few steps and demand the structure of this compound, the answer will be found in its reduction products ; for, if the free acid be treated with tin and hydrochloric acid, and the solution thus obtained is freed from tin by means of sulphuretted hydrogen, sulphanilic acid and amidophloroglucine may be extracted from the mixture.

The reaction that takes place here is as follows :

$$C_6H_4(\overset{4}{H}SO_3) - \overset{1}{N} = N - C_6H_2(OH)_3 + 2H_2 = C_6H_4(HSO_3)NH_2 + C_6H_2(NH_2)(OH)_3.$$

Therefore, as the HSO_3 group in sulphanilic acid is in the para

position, it is evident that it must hold the same position in parazosulphoxylbenzolephloroglucine.

This compound is of particular interest, as it is very similar to, and moreover, an isomere of azobenzolepyrogallol, the only difference being that the latter does not contain the HSO_3 group, while the former does.

Azobenzolesulphocresole, $C_6H_5-N=N-C_6H_2(HSO_3)CH_3(OH)$. If an alkaline solution of cresolesulpho acid be treated with an aqueous solution of diazobenzole nitrate, the result is a deep orange colored oily liquid. If this be allowed to stand for a short time, and then be treated with an excess of strong hydrochloric acid, the acid is by this means set free, and will after a short time crystallize in long brown needles, with a strong metallic lustre. It is quite soluble in alcohol, less so in hot water, to which it imparts an orange color. When treated with reducing agents, it splits up into aniline and amidosulphocresole, viz :

$$C_6H_5-N=N-C_6H_2(HSO_3)CH_3OH+2H_2=$$
$$C_6H_5NH_2+C_6H_2NH_2(HSO_3)(CH_3)(OH).$$

I have perhaps dwelt too long in the repetition of the compounds mentioned in my last paper, but there were certain points which I had omitted at first, and I therefore take this occasion of making them known.

We now come to some of my new dyes, and among the first may be mentioned

Dinitroxyazobenzoleorthoxysulphoxylbenzole, $C_6H_2(NO_2)_2(OH)-N=\overset{1}{N}-C_6H_3(\overset{2}{HSO_3})(OH)$. This compound lies intermediate between Griess' azosulphoxylbenzoleorthonitrophenol and my azobenzoletrinitroxybenzole, and may be obtained by treating one molecule of diazodinitrophenol with an alkaline solution of one molecule of phenolorthosulpho acid.

The proportions used in the experiment were : 10 grms of dinitroamidophenol were treated with 5 grms of strong HCl, and a solution of 3.5 grms of KNO_2 in 100 c.c. of water were added. The solution thus obtained is stirred for a short time, and then poured, little by little, into a solution consisting of about 5 grms of phenolsulpho acid, 2.5 grms of KOH, and 100 c.c. of water.

The mixture thus produced is allowed to rest for an hour, and the deep yellow-brown liquid is heated to boiling, and then saturated with strong hydrochloric acid. On cooling, the free acid crystallizes out in the shape of yellow-brown needles, with a metallic lustre. These are only sparingly soluble in hot and cold water.

The soda salt, $C_6H_3(NO_2)_2(OH) - N = N - C_6H_3(NaSO_3)OH$, may be obtained from the free acid by treating it with carbonate or hydrate of soda. It is somewhat more soluble in water than the free acid.

By reduction with strong reducing agents (as tin and hydrochloric acid), dinitroamidophenol and orthoamidosulphophenol are obtained, according to the following equation :

$$C_6H_3(NO_2)_2OH - N = N - C_6H_3(NaSO_3)OH + 2H_2 =$$
$$C_6H_3(NO_2)_2(OH)NH_2 + C_6H_3(NaSO_3)(NH_2)OH.$$

In this reaction, as, in fact, in all the others of this kind, the azo-group, —N = N—, is split in two, each nitrogen atom taking up two atoms of hydrogen, to form the amido compound. The compounds obtained in this reaction are of particular interest, as they clearly demonstrate the positions they hold.

Thus, we found that by reduction of dinitroxyazobenzoleortho-oxysulphoxylbenzole, that orthoamidosulphophenol was obtained, this clearly showing that the sulpho group is in the ortho position.

We next come to a compound I described a short time ago, but will here again mention, viz:

Dimethylazobenzoledinitroamidooxylbenzole, $C_6H_3(CH_3)_2 - N = N - C_6H(NO_2)_2(NH_2)_2OH$. If equal molecules of diazoxylolchloride and dinitroamidophenol are mixed together, and the solution be kept slightly alkaline, a deep red-brown liquid is thus obtained, which is then filtered to separate it from a black resinous substance formed at the same time. The filtrate is then slightly heated, and saturated with strong HCl + aq, which precipitates the coloring matter in the form of a red-brown crystalline powder. This is then collected on a filter ; washed and dried. It is sparingly soluble in cold, but more soluble in boiling water, and easily soluble in alcohol.

The aqueous solution is of a red-brown color, and the slightest trace of acid causes a marked change of color, namely, from red-brown to straw yellow. Owing to this phenomenon, I think the dye might be used to advantage as a test for acids. Its formation may be expressed according to the following equation :

$$C_6H_3(CH_3)_2 - N_2 - HCl + C_6H_2(NO_2)_2(NH_2)ONa =$$
$$C_6H_3(CH_3)_2 - N = N - C_6H(NO_2)_2(NH_2)OH + NaCl.$$

The free acid may be obtained by saturating the soda salt with a large excess of strong HCl.

Similar to Griess' azosulphoxylbenzoleorthonitrophenol is :

Azosulphoxylnaphthaleneorthonitroxybenzole, $C_{10}H_6(\overset{4}{HSO_3})—\overset{1}{N}=\overset{1}{N}—C_6H_3(\overset{2}{NO_2})OH$. This compound was produced by treating one molecule of diazonaphthionic acid, with an equivalent amount of orthonitrophenol. The two substances were mixed slowly, under constant stirring, and care was taken to keep the solution slightly alkaline until the end of the reaction. The deep red-brown solution, so obtained, was allowed to rest for a few hours ; then heated to boiling, and saturated with strong HCl, which threw down the free acid in a crystalline state.

Free acid. Red-brown microscopical needles, very soluble in water, with a red-brown color.

Soda salt, $C_{10}H_6(\overset{4}{NaSO_3})—\overset{1}{N}=\overset{1}{N}—C_6H_3(\overset{2}{NO_2})—OH$. Brown crystalline powder, easily soluble in water, and obtained from the foregoing by treating with NaOH + aq.

If we demand the constitution of this compound, the answer can readily be found in its reduction products ; for, if the dye be treated with reducing agents, as tin and hydrochloric acid, it splits up into paraamidosulphonaphthalene and orthoamidonitrophenol, thus showing that the sulpho group in the naphthalene nucleus, and the nitro group in the benzole nucleus, hold respectively the para (1 : 4) and the ortho (1 : 2) positions.

Up to the present time no attempts had been made to combine more than two sulpho groups in one compound, and these were either joined to three nuclei, as in $C_6H_4(HSO_3)—N=N—C_6H_3(HSO_3)OH$, or, they were bound to one nucleus, as in

$$C_{10}H_7—N=N—C_{10}H_4(HSO_3)_2OH.$$

Now, it occurred to me that possibly three HSO_3 groups might be combined, and thus afford a new field for investigation.

With this point in view, the following compound was produced :

Paraazosulphoxylbenzole-β-oxydisulphoxylnaphthalene,

$$C_6H_4(\overset{4}{HSO_3})—\overset{1}{N}=N—\beta\text{-}C_{10}H_4(HSO_3)_2OH.$$

This compound can be produced by several methods, giving compounds isomeric with one another. For instance, it might be prepared by combining diazosulphanilic acid with betanaphtholdisulpho acid ; or, by treating diazodisulphobenzole with betanaphtholmonosulpho acid ; or, by treating diazobenzole nitrate with betanaphtholdisulpho acid, and then sulpho conjugating, or *vice versa*.

All these methods would probably yield compounds similar to one another, as already stated, but the simplest method seemed to be the

first one mentioned, namely, the combining of diazosulphanilic acid with betanaphtholdisulpho acid.

If one molecule of diazosulphanilic acid be treated with an equivalent amount of betanaphtholdisulpho acid (made slightly alkaline), and allowed to rest for a few hours, the result is a deep orange-red solution. It is then slightly heated and saturated with strong HCl. On cooling, the free acid crystallizes out in pretty, orange leaflets, with a beetle green lustre. These are very soluble in water with a fine orange color.

The soda salt, $C_6H_4(\overset{4}{N}aSO_3) - \overset{1}{N} = N - \beta\text{-}C_{10}H_4(NaSO_3)OH$, is an orange colored powder and exceedingly soluble in water. It can be obtained from the free acid by treating it with sodic carbonate.

A lead salt was likewise produced by treating the free acid with plumbic acetate. Yellow powder, soluble in water with an orange color.

Tin and hydrochloric acid reduce this compound to paraamidobenzolesulpho acid and amidodisulphonaphthol, thus showing the position held by the benzolesulpho group in the formula. This compound then goes to prove that what we at first stated is possible, namely, the combination of three sulpho groups in one compound.

Isomeric with Griess' parazosulphoxylbenzole-β-naphtholsulpho-acid, $C_6H_4(HSO_3) - N = N - C_{10}H_5(HSO_3)OH$, is *azobenzole disulpho-naphthol*, $C_6H_5 - N = N - \beta\text{-}C_{10}H_4(HSO_3)_2OH$. This was obtained by treating an alkaline solution of the soda salt of β-naphtholdisulpho acid with one molecule of diazobenzole nitrate.

These two solutions were mixed under constant stirring, and the heavy orange colored precipitate thus formed, was collected on a filter, washed, dissolved in hot water, then precipitated with common salt, in the form of a soda salt, and finally dried.

The soda salt, $C_6H_5 - N = N - \beta\text{-}C_{10}H_4(NaSO_3)_2OH$, consists of little, orange colored leaflets, with strong green metallic lustre, and very soluble in water.

The free acid, $C_6H_5 - N = N - \beta\text{-}C_{10}H_4(HSO_3)_2OH$, is obtained from the soda salt by saturating an aqueous solution of the latter with an excess of strong HCl. Crystallizes in fern shaped leaflets, with strong metallic lustre; is very soluble in water and alcohol.

The barium salt, $C_6H_5 - N = N - \beta\text{-}C_{10}H_4Ba(SO_3)_2OH$, is obtained by treating a hot concentrated solution of the free acid with $BaCl_2$; orange colored leaves, sparingly soluble in water.

Reducing agents, as tin and hydrochloric acid, yield aniline and amidodisulphonaphthol.

Parazotoluole-β-naphtholdisulpho acid, $C_6H_4(\overset{1}{C}H_3) : \overset{4}{N} = N - \beta\text{-}C_{10}H_4(HSO_3)_2OH$. This pretty, scarlet dye was produced by combining equal molecules of diazotoluole nitrate and β-naphtholdisulpho acid together, the solution being kept slightly alkaline until the end of the reaction. The heavy red precipitate thus formed was collected on a filter, washed, dissolved in water, and precipitated again with common salt, in the form of a soda salt.

The soda salt, $C_6H_4(CH_3) - N = N - \beta\text{-}C_{10}H_4(NaSO_3)_2OH$, is produced as already stated. Red-brown crystalline powder, soluble in water with a fine scarlet color.

The free acid is obtained from this by treating with an excess of strong HCl. Red colored leaves, with strong beetle green lustre, and very soluble in H_2O.

The barium salt, $C_6H_4(CH_3) - N = N - \beta\text{-}C_{10}H_4(SO_3)_2BaOH$, is obtained from the free acid by treating with $BaCl_2$. Red crystalline powder, sparingly soluble in water.

Treated with reducing agents, paratoluidine and amidodisulphonaphthol are formed.

I have likewise produced the ortho (1 : 2) and meta (1 : 3) azotoluole-β-naphtholdisulpho acid in the same way as the previous compound, and it will not be necessary to describe the method of preparation.

They all resemble the para compound, more or less, and differ mostly in their shades ; one being yellower and the other redder. They are, likewise, pretty, scarlet dyes, and are easily soluble in water. On reduction, they yield respectively ortho and meta-toluidine and amidodisulphonaphthol. Similar in nature to Griess' parazosulphoxylbenzoleresorcine, and differing only in the color, is:

Parazosulphoxylnaphthaleneresorcine, $C_{10}H_6(\overset{4}{H}SO_3) : \overset{1}{N} = N - C_6H_3\begin{cases}OH\\OH\end{cases}$ This is produced by treating one molecule of diazonaphthionic acid with an equivalent amount of an alkaline solution of resorcine. The mixture thus obtained is allowed to stand for an hour, then heated to boiling and saturated with strong HCl. On cooling, the free acid crystallizes out, and may be purified by recrystallizing from water.

The free acid, $C_{10}H_6(\overset{4}{H}SO_3) : \overset{1}{N} = N - C_6H_3\begin{cases}OH\\OH\end{cases}$, crystallizes in dark brown needles, with metallic lustre, and is very soluble in water, with a fine red-brown color.

The soda salt, $C_{10}H_6(NaSO_3) - N = N - C_6H_3\begin{matrix}OH\\OH\end{matrix}$, is prepared from the foregoing by treating with NaOH. Brown crystalline powder, soluble in water. The constitution of the above named compound can be found in its reduction products, which are naphthionic acid and amidoresorcine.

Parazodibromsulphoxylbenzole-β-naphthol, $C_6H_2Br_2(\overset{4}{HSO_3}) - \overset{1}{N} = N - \beta\text{-}C_{10}H_6OH$. This interesting compound was obtained by allowing equal molecules of paradiazobibrombenzolesulpho acid and β-naphthol to react on one another; the solution being kept slightly alkaline until the end of the reaction. The mixture thus obtained was then heated slightly and saturated with HCl, which precipitated the free acid in the shape of an amorphous, orange-red mass. This was then washed, and crystallized from water.

The free acid is pretty soluble in hot water, less so in cold.

The soda salt can be obtained from the acid by treating with NaOH.

Reducing agents form amidotribrombenzolesulpho acid and amidonaphthol.

In concluding, I would say, that I hope next fall to be able to give a much fuller account of these compounds, with the analytical data.

XXIX.—On the Action of Light and Darkness on Standard Ammonium Chloride and Tannin Solutions.

By A. R. Leeds, Ph.D.

In the December number of the Proceedings of the American Chemical Society, for 1878, in a paper "On the Alteration of Standard Ammonium Chloride Solution, when kept in the Dark," I have given a brief resumé of the labors of MM. Schloesing and Muntz on the dependence of nitrification upon the presence of an organized ferment, and of the researches of Mr. R. Warington upon the necessity of darkness to the development of the nitrifying body. A standard ammonium chloride, kept in the dark, was found to contain a determinable amount of nitrites, and the titre of the solution to have diminished by an amount sufficient to unfit it for employment in Nesslerizing. These results were connected, by the author, with the transformation of the elements of ammonia into nitrous acid, under influence of fungoid growth in the dark. At the close of this article, it was stated that two methods of avoiding the change were naturally suggested: "1st. Keeping the ammonium solutions, not in

the dark, as generally happens, but in the light. 2nd. Addition of a drop of chloroform or carbon disulphide. The disulphide is inapplicable, speedily blackening the Nessler reagent. The chloroform in our possession was not entirely without action, but it was so slight as to be hardly appreciable when a drop was diffused in a considerable amount of water. 1 liter of standard ammonium chloride solution containing 0.25 mgrm H_3N per c.c., was divided into four parts, each part being placed in ¼-liter bottle. A piece of fungus found rapidly growing in a bottle of sodium acetate, was after repeated washing, put in each bottle. A drop of chloroform was introduced into two of the bottles, one of which has been placed in the light, the other in darkness. The bottles without chloroform have been similarly placed, and it is proposed, after a suitable interval, to determine what changes, if any, have occurred since then."

This has now been done, after a lapse of eighteen months, with the result of showing that no alteration has occurred in any one of them. Neither have the fungi placed in the solutions, changed in appearance or increased in size. The chloroform remained in the bottles as at first.

What difference then was there in the conditions under which the four last solutions were placed, as compared with the solution originally tried, which is adequate to account for the difference in the results? We know of none, except that the bottles containing the last four solutions were nearly filled with the liquid, and were sealed with paraffine. Apparently, the oxygen requisite for the transformation of the elements of ammonia into nitrous acid, under the influence of the growing organism in the dark, had been derived from the oxygen of the air contained in the partly filled bottle used in the original experiment. But in the later experiments, even in darkness and in the solution containing no chloroform, no change had occurred, the presence of free oxygen apparently being requisite for the conversion of the ammonia into nitrous acid, under the circumstances given.

With standard tannin solutions the results were quite different. At the time at which the ammonium solutions were prepared, a solution of tannin was also made, which contained in 1 liter of water, 1.482 grm of the acid. The liquid was divided into four portions, to each portion a similar fungoid growth was added, and they were then placed in liter bottles, securely paraffined, but, of course, with a space in each bottle above the liquid, containing air. Two bottles, one with two drops of chloroform, the other without, were placed at a south-

ern window, so as to be exposed for a considerable portion of the time to bright sunlight; two bottles similarly prepared, were put in darkness. As long as the bottles were left exposed to the sunlight for a portion of each day, the development of the fungus was extremely slow, and the liquid darkened very slightly. But at the end of fourteen months, these solutions were transferred to the diffused light of the laboratory, when the development of the fungus became much more rapid, and at the expiration of eighteen months, when all four bottles were opened, it was apparently little less in amount than that contained in the bottles which had remained in darkness during the entire interval. The odor of chloroform had disappeared from all four, showing that the chloroform, itself, had undergone decomposition, and what was still more striking, the amount of fungoid growth in the two bottles containing chloroform in light and darkness, was fully as great as the two similarly placed, but without chloroform. In fact, of the two bottles placed in the light, that containing the chloroform had lost the larger percentage of tannin, and, judging from this diminution, apparently had undergone the greater alteration. In the dark, however, the percentage of tannic acid in the bottle containing chloroform had not diminished to so great an extent as the bottle without, and the presence of the chloroform seemed, in this case, at least, to have exerted a somewhat preservative action upon the solution.

The conclusion to be drawn from both series of experiments is, that the circumstances most favorable to the indefinite preservation of standard solutions of this character, are *exposure to light, exclusion of air, and absence of germs of fungoid growth.*

XXX.—Action of Light on the Soluble Iodides, with the Outlines of a New Method in Actinometry.

By A. R. Leeds, Ph. D.

In the June number of the *Philosophical Magazine*, for 1879, I published an article with the above title, and gave an abstract of three preceding papers dealing with various parts of the same subject, viz.—"Upon the titration of hydrochloric acid for chlorine, and of sulphuric and nitric acids for hyponitric acid" (1st and 2nd papers, Proceedings American Chemical Society, **2**, 1878, and Journal American Chemical Society, **1**, 1879); also, "Upon the influence of light upon the decomposition of iodides" (Journal American Chemical Society, **1**, 1879). In the first of these papers I gave an account of the anomalous reaction which first attracted my attention to the subject, and led me to undertake a series of laborious quantitative determinations extended over an interval of three months. This was, that on titrating very dilute solutions of the acids with potassium iodide (1 c.c. acid to 1000 c.c. water), no change occurred immediately, but at the end of two hours an amount of iodine had been set free, corresponding to 0.42 c.c. of a standard sodic hyposulphite solution, in the case of the hydrochloric acid; to 0.28 c.c. with the sulphuric acid, and to 0.24 c.c. with the nitric acid. After decolorisation with the hyposulphite, slow change again set in, and a series of titrations, beginning with October 27th, 1878, and extended to December 5th, 1878, eleven in all, was given, showing that a constant source of change was operating upon the mixtures of very dilute acids and iodide—the summations of the changes effected during the interval being for the hydrochloric acid 1.23 c.c., for the sulphuric acid 5.17 c.c., and for the nitric acid 2.41 c.c.

This source of constant change was thought to be the diffused light of the laboratory, and in the second paper the results of testing this hypothesis, under a great variety of conditions and with many precautions as to purity of acids, iodides, etc., were detailed at length. In the third paper, the various phenomena noted were brought into reconciliation by recognising that *oxygen was essential to the reaction*, no change whatsoever occurring either in the dark or in the strongest sun-light during several days exposure, in case the presence of oxygen were rigorously excluded. This observation likewise explained the real difficulty at the root of the acrimonious controversy between Schoenbein and Fischer, Houzeau and Sauvage,* as to whether or

* Journ. f. pr. Chem., 1845, **34**, 492; Compt. Rend., 1868, **67**, 663, 714, 1138.

no perfectly pure potassium iodide, in dilute solution, is decomposed by free sulphuric acid.* The answer to this question, as determined by the author from the experiments quoted, was that either in light or darkness free acid will decompose potassium iodide if oxygen is present, even when the dilution is carried to the one four-thousandth part; but in case oxygen is absent, solutions of potassium iodide, with excess of free acid, and both solutions of considerable strength, may be kept for days in the dark or in strong sun-light, without a liberation of iodine.

Furthermore, all the cases of soluble iodides experimented upon, and the acids, organic acids as well, were shown to undergo a change represented by the general equation,

$$4MI + 4HA + O_2 = 4MA + 2H_2O + 2I_2,$$

where M indicates the monovalent basic, and A the monobasic acid radical.

In the earlier experiments (2d paper), before the indispensable co-operation of oxygen in the decomposition of the iodides, in presence of free acid, had been recognised, the law of change of the iodides in the dark appeared to be quite different from that operating when they were exposed to the light. In the former case, the amount of decomposition of the iodide was approximately proportional to the degree of concentration; in the latter, the reverse appeared to be true. This curious anomaly was done away with by the next step in the investigation: for in the preliminary trials, bottles of different forms and material had been used in holding the solutions; but it was evident that not only would the varieties in shape greatly alter the relative surfaces of exposure to the solar ray, but differences in tint of the glass (yellowish, white, pink, etc.) strongly affect the percentage of the transmitted actinic component of the beam. For these reasons, comparison tubes of uniform bore and dimensions (25 c.m. in length, 3 c.m. in diameter), such as the author has proposed in his color comparator,† all made of the same thin, perfectly colorless glass, were substituted. The anomalies now disappeared.

Before proceeding further, however, it was essential to determine to what extent the pure acids themselves underwent decomposition in the sunlight; and to this end, 50 c.c. of nitric acid, of sp. gr. 1.4, 50 c.c. of sulphuric acid, of sp. gr. 1.84, and 50 c.c. of hydrochloric

* See also Fischer, Pogg. Ann., **66**, 168; Journ. f. pr. Chem., **34**, 186; also Dulk, Journ. f. pr. Chem., **34**, 344, Criticism on Schoenbein's paper, "Some notes upon potassium iodide."

† Chem. News, **37**, 229.

acid, of sp. gr. 1.202, were hermetically sealed in bottles, and exposed at a south window from December 10th, 1878, to January 21st, 1879.

"At the end of this period, 1 c.c. of each was taken, diluted with 1 liter water, potassium iodide and starch water added, and allowed to stand for 24 hours in darkness." They gave, on titration:

1 c.c. HNO_3 = 14.80 c.c. $Na_2S_2O_3$.
1 " H_2SO_4 = None.
1 " HCl = "

This experiment was the first of a series, which are given at length in the articles referred to, by which it was shown that the decomposition of soluble iodides, in the presence of light and of free nitric acid, does not conform to the same general law which operates in the case of acids not of themselves decomposable by sun-light. The equations which explain the different deportment of nitric acid were given in full, and the necessity of rejecting its employment in making actinometric measurements was emphatically pointed out.

"This investigation suggested a convenient method for studying the variations in the actinic force of the solar ray, which was to determine the amount of iodine set free by its action, under identical conditions. In the following experiments, the first which were instituted in this direction, no attempt was made to determine absolute values. A series of comparison tubes, each containing 1 c.c. H_2SO_4, 1 c.c. KI, and 5 c.c. starch water, with the amounts of water specified, were exposed at times and during intervals given, upon a comparator, the frame of which was kept normal to the solar ray."

RELATIVE ACTION OF THE SUN'S RAYS (JAN. 22, 1879).

	20 c.c. H_2O	60 c.c. H_2O	100 c.c. H_2O
9.00– 9.30 A. M.	0.24 mgrm I	0.27 mgrm I	0.38 mgrm I
9.30–10.00	0.22	0.29	0.37
10.00–10.30	0.24	0.40	0.40
10.30–11.00	0.39	0.76	0.71
11.00–11.30	0.67	1.25	1.29
11.30–12.00	0.67	1.25	1.46
12.00–12.30 P. M.	0.55	1.25	1.54
12.30– 1.00	0.60	1.50	1.73
1.00– 1.30	0.50	1.13	1.31
1.30– 2.00	0.40 [clouded over]	0.75	0.92

CONTINUED, JANUARY 24TH.

	20 c.c. H_2O	40 c.c. H_2O	60 c.c. H_2O	80 c.c. H_2O	100 c.c. H_2O
2.30–3.00	0.125	0.24	0.33	0.38	0.40
3.00–3.30	0.110	0.18	0.24	0.27	0.28
3.30–4.00	0.070	0.10	0.12	0.13	0.12

It will be seen that the amounts of iodine liberated in the 40 c.c. solution and the 80 c.c. solution, are intermediate between those liberated in the solutions of 20 and 60, and 60 and 100, respectively. Moreover, the determination of the liberated iodine is so easily made, that we possess in this method a convenient form of actinometry, lending itself readily to various practical applications. The chlorine-hydrogen method of Draper, which received at the hands of Bunsen and Roscoe the various instrumental refinements essential to accurate quantitative results, requires a corresponding complexity of apparatus and nicety of manipulation, and is therefore carried into execution with difficulty by the working chemist. The method just described needs little or no apparatus beyond that essential to any well equipped laboratory.

The next question investigated (3d paper), was "*to determine whether a change of base influenced the rate of decomposition in the sun-light when the same acid was employed; or, with the same base, when different acids were used.*"

In solving this question, the intention was to employ chemically equivalent solutions of the acids, but, by an error in the calculation, the solutions actually employed in this and the subsequent parts of the work were of such strength, that 1 c.c. of the sulphuric acid corresponded to 0.43 c.c. of the hydrochloric, and to 0.504 c.c. of the nitric acid. The experiments were made and the wood-cuts executed before the error was discovered, which accounts for the publication of the results as given in the articles alluded to, and from which only I shall quote in the present communication. But, whilst I was unable at that time to undergo the expense of having new plates made, and published these somewhat imperfect results just as they stood, I repeated in March, 1879, the experiments with truly equivalent solutions, and shall in a subsequent paper make them known, with appropriate graphic representations.

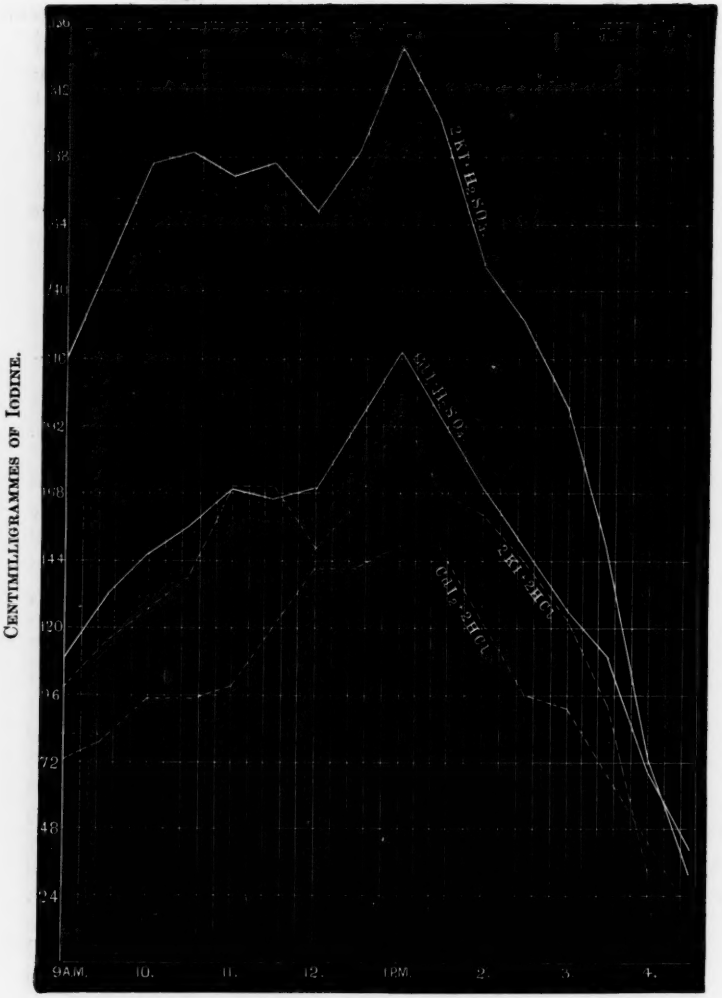
In all the earlier trials starch-water was used in making up the solutions in the comparison tubes to the desired volume, since "*the supposition had been, that its affinity for the liberated iodine, though feeble, had nevertheless been one of the agencies at work in determining the fact of a decomposition.*" But a series of trials is given (3d paper) with the iodides of potassium, cadmium and lithium, and with the three mineral acids, which showed that in every instance the amount of decomposition was greater when the addition of starch was omitted. The dense precipitate of starch iodide suspended in the tubes, cut off to a large degree the action of the light upon the solutions. Moreover, the disturbing effect of such an opaque pre-

cipitate was so great, that the striking quantitative relationships existing between the amounts of iodine liberated by the unequal chemism of different acid radicals for the same metallic base, were not made manifest, until by doing away with the starch, the reactions were rendered normal. The most important instance of this constant difference of chemism which as yet has been worked out, is that between $\frac{1}{2}H_2SO_4$ and Cl in the presence of KI, CdI_2, NH_4I and LiI solutions exposed to sun-light.

The progress which had been made in solving the question above italicised, will be gathered from an examination of § VII (3d paper), "*Upon the actinometric determination of sun-light*," which begins by stating that "in order to compare the decomposition effected by the sun-light, after passing through various thicknesses of the earth's atmosphere, and the relative amounts of iodine set free under these circumstances when different salts were employed, the determinations summarized in the accompanying table were made." The day was unusually brilliant and unclouded from beginning to close. The amounts of iodine are given in centimilligrammes. The solutions were all made up to 100 c.c.

ACTINOMETRIC DETERMINATIONS, February 27th, 1879.

REAGENTS.	9 A.M.–9.30	9.30–10	10–10.30	10.30–11	11–11.30	11.30–12	12–12.30	12.30–1 P.M.	1–1.30	1.30–2	2–2.30	2.30–3	3–3.30	3.30–4	4–4.30	4.30–5	MEANS
1 c.c. H_2SO_4 + 1 c.c. KI	215	250	285	290	280	285	270	290	325	300	250	225	200	155	75	35	233
1 c.c. HCl + "	100	115	125	140	170	170	155	165	200	170	160	145	125	90	35	23	131
1 c.c. H_2SO_4 + 1 c.c. CdI_2	115	130	145	155	170	165	170	195	220	195	170	150	130	110	70	43	146
1 c.c. HCl + "	75	85	100	100	105	120	140	140	150	150	120	95	90	65	35	20	99
1 c.c. H_2SO_4 + 1 c.c. LiI	120	130	135	145	160	150	160	170	155	145	150	140	125	105	65	43	131
1 c.c. HCl + "	75	80	95	100	100	100	110	120	120	110	100	75	70	50	30	18	84
1 c.c. H_2SO_4 + 1 c.c. NH_4I	130	140	155	165	180	170	180	190	195	180	170	150	120	105	70	45	146
1 c.c. HCl + "	85	95	100	100	115	115	115	120	115	115	110	85	90	60	30	18	92



February 27th, 1879. Hours of the day.

Unfortunately, as before stated, the solutions were not chemically equivalent, 1 c.c. of the H_2SO_4 corresponding to 0.43 c.c. HCl, and the potassium iodide solution being of 20 per cent., the other iodides of 10 per cent. But if we multiply the means of the numbers of centimilligrammes of iodine, in each case set free in the presence of

the sulphuric acid, by 0.43 (the number expressing the relative strength of the hydrochloric acid), and divide the products into the amounts of iodine liberated by the hydrochloric acid, we obtain the following ratios :

H_2SO_4 + KI = 233 × 0.43 = 100
HCl + " = 131 × 1.00 = 131, or 1 : 1.31
H_2SO_4 + CdI_2 = 146 × 0.43 = 64
HCl + " = 99 × 1.00 = 99, or 1 : 1.55
H_2SO_4 + LiI = 131 × 0.43 = 56
HCl + " = 84 × 1.00 = 84, or 1 : 1.50
H_2SO_4 + NH_4I = 146 × 0.43 = 63
HCl + " = 92 × 1.00 = 92, or 1 : 1.46
Mean ratio, for 128 experiments, = 1 : 1.45

We have here a set of ratios obtained with 128 solutions exposed during the course of one day, under identical circumstances in each corresponding experiment, of time, of exposure, temperature, surface, intensity and quantity of light, size and nature of vessel, etc. The ratio 1/1.31, obtained with the potassium iodide solution, is retained, though it might without violence be thrown out, inasmuch as this solution contained 20 per cent. of the iodide, the other three but 10 per cent. of their respective iodides. We have reason, therefore, for bringing forward the hypothesis that the chemism of the Cl radical, as compared with that of the $\frac{1}{2}SO_4$ radical, and as made manifest by the amount of metathetical decomposition taking place in sun-light in mixtures of their hydrogen salts with the iodides of certain metallic radicals, may be expressed by a certain ratio. And without claiming any thing further than the suggestion of some quantitative relationship, not as yet fully apprehended, this ratio might be expressed as a law of specific actinic forces under the formula :

The chemism of the chlorine radical is to that of the $\frac{1}{2}SO_4$ *radical* (*measured by the relative amounts of iodine liberated by each respectively, in solutions of the metallic iodides exposed to sun-light*), *as* 1.45 : 1. This formula holds good, as was shown in the unpublished actinometric determinations made March 26th, 1879, for rigorously chemically equivalent solutions of the acids. But the ratio requires change when the actinic power emanates from a different source, the magnesium lamp for example. This will be forcibly shown further on. A similar law appears to be true of the amounts of iodine set free from iodides of different metals, when exposed to the action of sun-light in presence of the same acid—these amounts standing in definite ratios, one to another.

Before leaving this diagram, I wish to point out the remarkable depression in the $2KI + H_2SO_4$ curve, and the $CdI_2 + H_2SO_4$ curve, between the hours of 11 A. M. and 1 P. M. As soon as this tendency was noted, I naturally anticipated the passage of some visible mist or haze across the sun. Such, however, was not the case, the sky appearing just as brilliant and blue during this interval as before and after. I deemed it not improbable that this absorption of the actinic component of the solar ray, was due to the passage of some mass of aqueous vapor, or some other alteration in the physical or chemical constitution of an interjected atmospheric layer, which, though invisible to the sense of sight directly, had been written down in the sensitive chemical fluid by the blurred tracing of the actinic rays. This, indeed, was an animating thought—that we possess in the undulations of the solar beam, which are too rapid to affect vision, a delicate probe to reach down through various parts and thicknesses of the earth's atmosphere, and to tell what alterations of constituents may be taking place there. To test this idea, a set of experiments was undertaken upon the absorbing action of vapors, gases, etc., upon the chemical component of the solar, electric and magnesium light, under known conditions in the laboratory, prior to their extension to an actino-chemical analysis of the atmosphere. The circumstances narrated below will cause the publication of the results, though in a somewhat incomplete state, at once.

§ IX (3d paper) was devoted to the "*Influence of heat upon the decomposition of the iodides.*" Three series of trials were instituted in this direction. The first was made before the *hauptrolle* played by oxygen in these decompositions, was recognised. It consisted in noting the intervals through which the same amounts of potassium iodide, sulphuric acid, and starch-liquor, diluted with 20 c.c., 60 c.c., and 100 c.c., water, ran through a scale of colors (very faint rose, faint rose, rose, violet and blue), as the temperature rose from 30° to 95°. On continuing the heating, the colors disappeared in the inverse order, due to the gradual conversion of the indicator into dextrine, under the influence of the dilute acid.

The second series of trials was upon the "Effect of heat in closed flasks." Of course, the use of starch was abandoned in these and subsequent trials. The final result obtained, to quote from the original paper, was that—"In other words, when the potassium iodide was diluted 600 times, and heated nearly to the boiling point (93°), in a closed flask, for six hours, the amount of iodide set free was so small that it could not be estimated; and when diluted 1200 times, no change whatever took place."

The third series was upon the "Effect of heat in flasks entirely deprived of air." The previous displacement of the air held in solution in the liquids, was effected by a long-continued current of carbonic anhydride. When this was done, the solutions of potassium iodide, both with sulphuric and hydrochloric acid, were heated for two hours to a temperature five degrees above the boiling point of water, without any liberation of iodine whatsoever. Similar acidified solutions, heated to the same temperature, in contact with air, turned *yellow immediately.*

§ IV (3rd paper) was upon the "*Decompositions effected by the electric light.*" The experiments were performed by arranging the solutions in comparison tubes, so as to form the sides of a cylinder with the focus of the electric light at the geometric centre. "The electric arc was taken between carbon points, and was produced by electricity generated with a dynamo-electric machine run by steam power, its illuminating capacity varying during the course of the experiment, according to photometric measurements made by Prof. Morton and Mr. Beckmayer, between 7000 and 7500 candles." Reducing the observations in the same manner as was done above with the actinometric determination of sun-light, we have, the results being given in mgrms of iodine:

ACTINOMETRIC MEASUREMENT OF ELECTRIC LIGHT.

	15 min	20 min	7½ min	MEANS.	RATIOS.
1 c.c. H_2SO_4+1 c.c. KI	1.65	3.90	3.00	$2.85 \times 0.43 = 1.22$	
1 c.c. HCl + "	1.05	3.40	2.00	$2.15 \times 1.00 = 2.15$	1 : 1.76
1 c.c. H_2SO_4+1 c.c. CdI_2	1.80	3.15	2.25	$2.40 \times 0.43 = 1.03$	
1 c.c. HCl + "	1.25	2.50	1.35	$2.02 \times 1.00 = 2.02$	1 : 1.96

The same remarks are true of the chemical decompositions of the iodides effected by the electric-, as when the decomposition resulted from the sun-light. But the amount of iodine liberated in each trial was relatively several lines greater, and the coefficient of chemical energy of the chlorine radical, 1.86 instead of 1.46. This exaltation of the relative chemical energy of the chlorine under the influence of the electric light, will be still more strikingly exhibited when the results obtained with rigorously equivalent solutions are published.

§ V (3d paper) was devoted to the "*Comparison of effects of sun-light and electric light, after passing through absorbing media.*"

The experiments were performed as usual, except that the comparison tubes were surrounded by a layer, 3 c.m. in thickness, of the absorbing medium: ammoniacal solution of copper for the blue, neutral potassium chromate for the yellow, and fuchsine for the red. They were made of such strength that the outlines of an object could be seen through them with equal distinctness, though in each case feebly. Reducing the observations as before, we have:

EFFECT OF ABSORBING MEDIA.

		Sun-light (1 hour).	Ratios.	Electric Light (1 hr.)	Ratios.
Blue	1 c.c. H_2SO_4	$2.38 \times 0.43 = 1.02$	1 : 2.2	$6.00 \times 0.432.5 = 8$	1 : 1.7
	1 c.c. HCl	$2.22 \times 1.00 = 2.22$		$4.50 \times 1.00 = 4.50$	
Yellow	1 c.c. H_2SO_4	$0.67 \times 0.43 = 0.33$	1 : 1.4	$0.50 \times 0.43 = 0.22$	1 : 2.0
	1 c.c. HCl	$0.45 \times 1.00 = 0.45$		$0.45 \times 1.00 = 0.45$	
Red	1 c.c. H_2SO_4	$1.53 \times 0.43 = 0.66$	1 : 1.3	$4.95 \times 0.43 = 2.15$	1 : 1.5
	1 c.c. HCl	$0.83 \times 1.00 = 0.83$		$3.00 \times 1.00 = 3.00$	

The fact most striking in this tabular view is, that while the greater strength of the actinic component of the electric beam is very manifest, the *yellow* absorbing medium absorbed 85 per cent. of the actinic energy which was transmitted through the blue solution, and 83 per cent. of that which passed through the red. Of the actinic energy of the sun-light, 32 per cent. of that which passed through the blue was absorbed by the yellow, and 50 per cent. of that going through the red. But the actinic energy of that part of the *sun's* actinism which passed through the fuchsine, was but one-third of that of the *electric light.* I have said actinic energy, rather than actinic rays, because the absorption spectra for the invisible part of the spectra of the sun and electric light, possessed by these substances, has, so far as I know, not been mapped. To quote from the original: "Better to understand what occurs in this instance, a study of the absorption spectra (chemical) of the media, and of the various iodides in the several portions of the sun and electric light, has been entered upon" (February, 1879).

§ VI (3d paper) was upon the "*Decomposition effected by the magnesium light.*" Reducing the observations (one set obtained by an hour's exposure) to the same standard as before, we have:

					Ratios.
1 c.c. H_2SO_4 + 1 c.c. KI	= 0.050 mgrm I	× 0.43	= 0.0215		
" HCl + "	= 0.075 "	× 1.00	= 0.0750	1 : 3.5	
" H_2SO_4 + 1 c.c. CdI_2	= 0.035 "	× 0.43	= 0.0150		
" HCl + "	= 0.050 "	× 1.00	= 0.0500	1 : 3.3	
" H_2SO_4 + 1 c.c. LiI	= 0.040 "	× 0.43	= 0.0170		
" HCl + "	= 0.050 "	× 1.00	= 0.0500	1 : 3.0	
" H_2SO_4 + 1c.c. NH_4I	= 0.060 "	× 0.43	= 0.0260		
" HCl + "	= 0.070 "	× 1.00	= 0.0700	1 : 3.0	

The results were very surprising for their smallness, because the experiments were arranged in the same way as with the electric light, the focus of the lamp being at the geometric centre of a cylinder, formed by the comparison tubes, the cylinder being of 6 in. radius. For, while to the eye, the white light of the burning magnesium was painful, the chemical decomposition effected by it was but the $\frac{1}{775}$th part of that effected by the electric light during the same interval, and but $\frac{1}{73}$d part of that effected by the sun. The coefficient of comparative chemical energy exhibited by the chlorine atom under these circumstances, is 3.2 as against 1.86 in case of the electric light, and 1.45 in that of the sun.

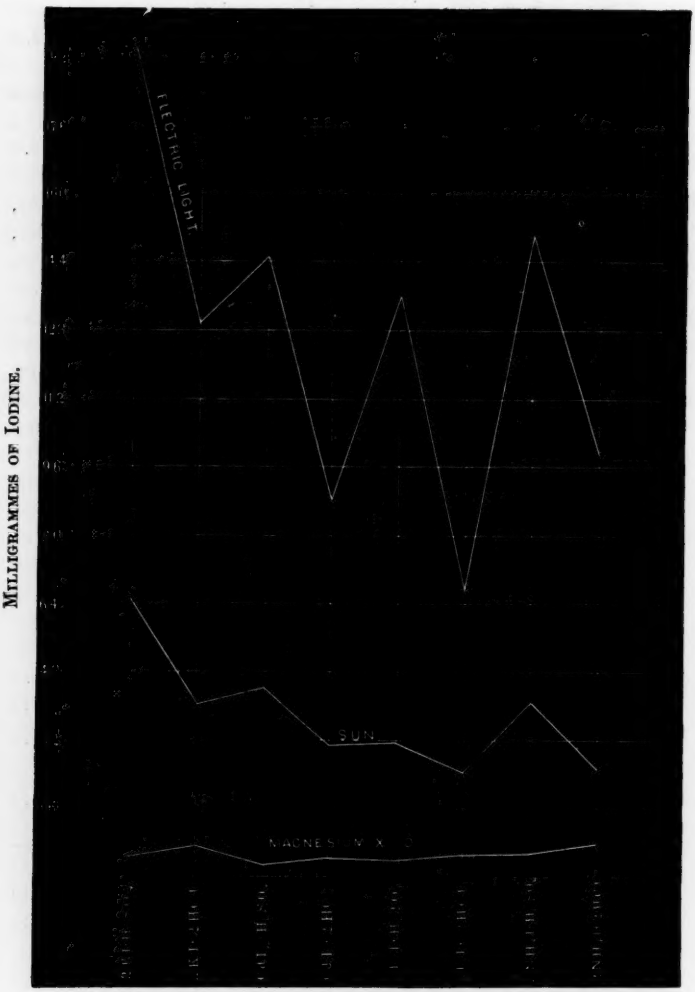
§ VIII (3d paper) was devoted to the "*Comparison of actinic intensities for equal times.*" Reducing these observations as before, the amounts of liberated iodine being given in mgrms, we have:

DECOMPOSITION DURING EQUAL TIMES (1 hour).

REAGENTS.	ELECTRIC LIGHT.		SUN.		MAGNESIUM.		RATIOS.
	Obs'rd	Reduced	Obs'rd	Reduced	Obs'rd	Reduced	
H_2SO_4 + KI	19.5	12.38	6.5	2.3	0.050	0.022	560 : 100 : 1
HCl + "	13.0	13.00	4.0	4.0	0.075	0.075	173 : 53 : 1
H_2SO_4 + CdI_2	14.6	6.28	4.4	1.9	0.035	0.015	420 : 126 : 1
HCl + "	8.8	8.80	3.0	3.0	0.050	0.050	176 : 60 : 1
H_2SO_4 + LiI	13.7	5.99	3.1	1.3	0.040	0,017	350 : 83 : 1
HCl + "	6.5	6.50	2.4	2.4	0.050	0.050	130 : 48 : 1
H_2SO_4 + NH_4I	15.0	6.45	3.9	1.7	0.060	0.026	248 : 65 : 1
HCl + "	9.8	9.80	2.3	2.3	0.070	0.070	140 : 33 : 1
Means of H_2SO_4							395 : 94 : 1
" HCl							155 : 50 : 1
Means of all							275 : 72 : 1

These phenomena are graphically represented in the following diagram, the observed results being taken for abscissas and ordi-

nates, and the magnesium ordinates multiplied by 10 to bring its curve up into the field of view.



SUMMARY.

I.—The part played by oxygen is the essential fact in the decomposition of soluble iodides in acidified solutions; no decomposition taking place either in darkness or in the strongest sun-light, in case

oxygen is absent. The principal exception to this rule is when nitric acid is employed.

II.—In case oxygen is present, the reaction takes place according to the equation, $4MI + 4HA + O_2 = 4MA + 2H_2O + 2I_2$, where M stands for any monovalent basic radical, and A a monobasic acid radical. This is true of the solutions both in darkness and in light.

III.—In case sufficient oxygen is present to permit of a normal reaction, the amount of iodine liberated in the darkness is strictly proportional to the degree of concentration, up to the limit to which the above equation is true. In the light, the same law holds good; the surface of exposure, the quantity and intensity of the light remaining the same, the degree of concentration the variable.

IV.—In case sufficient oxygen is present, and the degree of concentration is fixed, the amount of iodine liberated increases in the same ratio as the time of exposure to the light. There is likewise much reason for supposing that it stands in a similar numerical relation to the number and intensity of the chemical rays falling upon the solution.

V.—With a constant actinic energy, and with equivalent solutions of acids, the amounts of iodine liberated differ by constant quantities, which appear to be coefficients of comparative chemical energy of the acid radicals under these conditions. A similar law appears to apply to the various basic radicals of the iodides in the presence of the same acid.

VI.—In the absence of oxygen no decomposition takes place either in light or darkness, nor in dilute nor quite strong solutions, when the solutions are *heated* for hours to a temperature 5° above the boiling point of water. In the presence of oxygen, instantaneous and abundant decomposition sets in at this temperature, and correspondingly at lower temperatures.

Applications of the iodo-acid method. 1st. To determine the amount of chemical work done by the sun's rays while passing through various layers of the earth's atmosphere, either during each hour in the same day at any given place, or at different places for each day and season of the year. Curves representing such actinometric measurements at Hoboken, for January 22nd and 24th, 1869, and February 27th, 1879, are given.

2d. To determine the absorptive coefficients for the chemical rays of the sun (or other powerfully actinic light) of various gases, vapors, etc., under known conditions in the laboratory, and then apply the knowledge thus obtained to an actino-chemical analysis of the atmosphere.

3d. To map the actinic spectra of the sun, electric, magnesium, and other powerfully actinic illuminants, and the absorption bands for the invisible rays, when the light from these sources passes through solids, mineral and organic compounds, in dissolved or liquid form, and vaporous or gaseous bodies.

4th. To determine the comparative coefficients of combining and decomposing power of elements in compounds subject to metathesis, by actinic forces, and to find these actino-equivalents for invisible rays of various refrangibility.

Besides the extended account published in the June number of the *Philosophical Magazine*, for 1879, I sent about the same time to different gentlemen in Europe, and among them, directed to his address in Manchester, to Dr. R. Angus Smith, reprints of the three original articles. Nothing then could exceed the surprise I felt when I saw an article published in the *Chemical News* for May 7th, 1880, being "A paper read before the Royal Society, April 29th, 1880," under this gentleman's name, in which beneath the title "Measurement of the actinism of the sun's rays and of daylight," he gives a meagre account of the process, which in every point runs parallel with and coincident with my own, except in several vital omissions. This, I think, will appear on consideration of the following resumé of Dr. Smith's work. He states—"The fundamental fact is, that when iodide of potassium in solution is treated with nitric acid, so small in quantity as to cause no change of color in dull diffused light, a change takes place when the same mixture is brought into clear light; iodine is set free and the solution becomes yellow. The amount of iodine freed can be titrated with great exactness, by the use of hyposulphite, as is well known. In these two facts lies the whole process; the first is the new part, the second makes the first quantitative, and it is, of course, part of the novelty."

We most cheerfully admit the novelty exhibited by Dr. Smith in selecting, of all others, nitric as the acid forming part of the fundamental fact of the process as he states it. For it is true, that in the 128 determinations of the iodine liberated from four iodides in the presence of sulphuric and hydrochloric acids, and titrated by the use of standard (1 c.c. = 5 mgrms I) sodic hyposulphite and $\frac{1}{10}$ standard, these 128 determinations being all made in one day, February 27, 1879, I did not use nitric acid. And the reason for its omissions are stated in many places (2d and 3d papers). For while the reaction in dilute solution (Eq. 2, § X, 3d paper) for sulphuric acid is $4KI + 2H_2SO_4 + O_2 = 2K_2SO_4 + 2H_2O + 2I_2$, and for hydrochloric acid

(Eq. 6), $4KI + 4HCl + O_2 = 4KCl + 2H_2O + 2I_2$, that for nitric acid is not only the normal one of $4KI + 4HNO_3 + O_2 = 4KNO_3 + 2H_2O + 2I_2$ (Eq. 3), but the secondary ones of $2HNO_3 = N_2O_4 + H_2O + O = 2HNO_3$ (in sun-light) $= N_2O_3 + H_2O + O_2$ (Eq. 4),* and $2KI + 2HNO_3 + N_2O_3 = 2KNO_3 + H_2O_2 + N_2O_2 + I_2$ (Eq. 5). It had been abundantly demonstrated by many experiments (what was well known before) that nitric acid of itself, no iodides being present, spontaneously breaks up into one or more lower oxides of nitrogen and free oxygen, in the sun-light, and generates in the body of the solution itself an abnormal supply of that oxygen, which is the fundamental factor in these cases of actino-chemical change. Later on, Dr. Smith suspects that the nitric acid itself, in dilute solution, was subject to decomposition, and substitutes for his new and fundamental fact, the use of sulphuric acid. This I shall venture to assure Dr. Smith certainly is not new, inasmuch as he will find it stated at great length, *Philosophical Magazine*, for 1879, 396. Neither, however, is it fundamental, for an equivalent amount of hydrochloric acid possesses a greater coefficient of iodine-liberating power when placed in an actinic field.

Dr. Smith furthermore states: "3. It is known that strong acid liberates iodine; weak acid does so after a long time, but the process is hastened by light." This generalized statement cannot fail to lead to confusion and error, if left unqualified by a precise idea of the conditions under which it is false, and those under which it is true: for when oxygen is excluded,† "decomposition of an acid solution of potassium iodide occurs only after the concentration has attained to some point between one-third and one-tenth the weight of the water employed." The acidifying body, referred to in the experiments quoted, is sulphuric acid, and a more precise limit of concentration is not given, because of the undue multiplication of trials thereby entailed. But decomposition ensues, in this instance, from the production of an entirely different set of conditions on the attainment of the limit, and the sulphuric acid splits up, thereby furnishing the essential oxygen by an endo-chemical change. Instead of $4KI + 2H_2SO_4 + O_2 = 2K_2SO_4 + 2H_2O + 2I_2$ (Eq. 2, § X, 3d paper), the equation given for this case is

$2KI + 2H_2SO_4 = K_2SO_4 + 2H_2O + SO_2 + I_2$ (Eq. 1).

* Gay-Lussac states that the decomposition is into nitrous acid. He adds that nitric acid, whose density is as low as 1.3235, is not decomposed by light, except in the presence of a certain quantity of concentrated sulphuric acid, when even the most dilute acid undergoes change.—Ann. Chim. Phys., 1816, 397.

† Upon the detection and estimation of nitrous acid in potable waters, acids, &c., with potassium iodide, by the Author: Chem. News, Aug. 8th, 1879, 61.

With regard to the statement, that weak acid liberates iodine after a long time, but the process is hastened by light, it appears to the author that herein is contained the fundamental proposition of Dr. Smith's labors, and that, as such, it demanded elaborate experimental verification. For although, in a qualified sense, the proposition is true, yet the working out of the exact conditions under which it holds good, constituted the preliminary and most laborious portion of the work performed by the author, in the three papers previously referred to, and in others following them. Moreover, if these facts and conditions be so well known, and generally accepted, that a method of actinometry might be founded upon them without further independent proof, yet the evidence of their being commonly ignored is to be seen in the very frequent publication of erroneous observations and conclusions, concerning processes in which soluble iodides are concerned. Let me instance again the bitter controversy between Schoenbein and Fischer, Houzeau and Sauvage, as to the *fact* of a dilute potassium iodide solution being decomposed in the presence of very dilute sulphuric acid. More striking still, the universal employment of an acidified solution of potassium iodide for titrating a current of air or oxygen, carrying with it ozone, or ozone and peroxide of hydrogen. It is but a few weeks ago since, in certain experiments instituted to discover whether or no ozone is given off by the slow oxidation of phosphorus in moist air, the most abundant reaction for ozone was obtained when the current of ozonised air was heated to 200°, before its passage into an acidified solution of potassium iodide ; but at a temperature of 200°, 97 per cent. of the ozone present in ozonised air or oxygen is *destroyed at once*, and the residue very speedily.*

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* Peroxide of hydrogen and ozone, Chem. News.

NOTE.—It is earnestly to be hoped, in the controversy alluded to in this reference, that the indisposition, either to become acquainted with, or to recognise the labors of preceding investigators, will not be continued. I would respectfully ask the gentlemen concerned to refer as far back as 1840, to the article by Schoenbein, entitled, "Researches on the nature of the odor given off by certain chemical reactions" (Compt. Rend., **10**, 706; Ann. Elec., **6**, 108); also to this article upon the "Production of ozone by chemical means" (1844) (Arch. de l'Elec., **4**, 333, 454). Let me ask them to read, likewise, the critique, by Fischer (Berl. Jahresb. f. wissensch. Kritik, 1844), upon Schoenbein's pamphlet, "Ueber die Erzeugung des Ozons auf chemischen Wege," followed, as it was, by a second attack from the savan of Breslau (Schles. Gesell. Uebersicht, 98, 107; Pogg. Ann., **66**, 163; Journ. pr. Chem, **35**, 351), in which he advanced the hypothesis, that the ozone discovered by Schoenbein was probably a peroxide of hydrogen. We have seen how, 35 years

If more evidence were needed to show that the spontaneous decomposition of a soluble iodide in presence of dilute acid and oxygen, is a fact generally ignored, it is to be found in the tests recommended in Fresenius' Qual. Analysis for the detection of free chlorine in hydrochloric acid, and of hyponitric in sulphuric acid—the latter "when diluted with twenty parts of water, must not impart a blue tint to a solution of iodide of potassium mixed with starch paste.*" But if the trial be made in an atmosphere of carbonic acid, care being used to expel previously all traces of air in reagents and in the

later, this hypothesis was again brought forward by Mr. Kingzett, without reference to the battle of these illustrious teachers of a past generation, and without comment upon Schoenbein's reply to Fischer's attack (Journ. f. pr. Chem., **34**, 492; Pogg. Ann., **65**, 190), Mr. Kingzett asserting that "*there is no known process of slow oxidation, which has been established to produce ozone,*" and that the substance formed in the aerial oxidation of phosphorus is peroxide of hydrogen. Whilst the controversy was raging in Germany between Schoenbein and Fischer, it was opened in England by Prof. Williamson's "Researches on ozone" (Chem. Soc. Mem., **2**, 395; Liebig Ann., **54**, 127; Phil. Mag., **27**, 372; Compt. Rend., Mar., 1845)—in which Dr. Williamson states, as the result of elaborate experiments, performed with exceeding care, that there were reasons for believing in the existence of two kinds of ozone: one the ozone given off in electrolysis, and which he regarded as a higher oxide of hydrogen, differing from the previously well known peroxide; and the other formed by the action of phosphorus on moist air. I cannot regard the rejoinder of Schoenbein (Pogg. Ann.. **66**, 292; Phil Mag., **27**, 450)—in which he showed 1st, that the chemical and physical properties of ozone are not the properties of peroxide of hydrogen; and 2d, that whatever might be the true nature of ozone, the gaseous matter obtained in the electrolysis of water, was in all respects identical with that formed by the action upon air of moist phosphorus—otherwise than as a masterpiece of cogent reasoning, and as an argument *for the identity of ozone from whatever source produced*, even at the present day unsurpassed. His eminent English antagonist never replied, and the doctrines of Schoenbein on this point passed into the text books, and remained there without a dissenting voice until, unsupported by any show of evidence that he had performed more precise experiments on his own part, or that he had in any particular demonstrated errors in the work of those whom he so assertively attacked, Mr. Kingzett pronounced them false.

Perhaps even more surprising, as certainly more novel, are the polemical methods adopted by Prof. McLeod. For, stepping down unasked of the two principals in the fight, into this particular arena of controversy, and without even the fine courtesy, traditional to a free lance, of previous salutation by name or token of reference, Prof. McLeod proceeds forthwith to demolish his two antagonists, and makes them both to be in error. This too, without invoking, by *as much as a single foot note*, the shades of the mighty contestants, who took part in the much greater battle fought on these points more than a quarter of a century before, to be spectators of the fray!

* Fresenius' Qualitative Analysis, 6th Ed., 32, 35.

dilute acid solution, the test and estimation of percentage may be satisfactorily performed.* A like proof may be found in the customary mode of applying Trommsdorf's method for the detection and estimation of nitrous acid in potable waters.† When the zinc-iodide-starch reagent and water, under examination, are left without previous expulsion of dissolved oxygen, the amount of iodine set free by spontaneous decomposition, even in the diffused light of a laboratory, may much exceed the total quantity of nitrous acid present. In truth, an amount admitting of quantitative determination may apparently be found, when, as examined by the Griess test (meta-diamidobenzole), not a trace of nitrous acid is actually present.

Finally, examine in this connection the admirable memoir of Schoene, "upon the quantitative estimation of hydrogen peroxide.‡" For in one series of trials, this investigator employs concentrated solutions of potassium iodide and hydrochloric acid to determine minute amounts of hydrogen peroxide dissolved in different quantities of water. In another series, the solutions were boiled in contact with the air, and the amounts of hydrogen peroxide found, which in most trials exceed the quantities taken, corrected by a figure obtained by boiling similar solutions, *but containing no hydrogen peroxide*, during an equal interval. True values, it appears to me, might have been found in both series of trials, had the experiments been performed with the exclusion of every trace of oxygen from the solutions. It is the more surprising, inasmuch as in the same article, this most careful experimenter calls attention to the method of Gernez‡ for freeing solutions of oxygen by a current of an indifferent gas, and the experiments of Baumert, § Payen ‖ and Lehmann, ¶ upon the decomposition of hydriodic acid by oxygen.

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* Chem. News, 63; ibid, 62.

† Zeitschr. f. anal. Chem., **18** (1879), 144.

‡ Compt. Rend., **63**, 883; Zeitschr. f. Chem. [2], **2**, 717.

§ Pogg. Ann., **99**, 92.

‖ Compt. Rend., **62**, 254.

¶ Arch. Pharm. [3], **2**, 25; Chem. Centr., 1873, 152.

NOTE.—The historical aspect of this important question is of great interest. In 1853, Baumert thought he had succeeded in proving the existence of two kinds of ozone; the one prepared by the electric discharge, which he regarded as allotropic oxygen; the other, afforded by the electrolysis of acidulated water, to which he assigned the formula H_2O_3, teroxide of hydrogen (Breslau, Schles. Gesell. Verhandl. Uebersicht, 24; Ann. de Chim. et Phys., **39**, 477; Journ. f. pr. Chem., **59**, 350; Journ. de Pharm., **24**, 381; Phil. Mag., **6**, 51; Ann. der Chem. u. Pharm., **88**, 221; Pogg. Ann., **89**, 38). He passed the electrolytic oxygen, evolved in such a manner as to exclude the presence of hydrogen, through a

Dr. Smith goes on to state: "4. Heat, even to the boiling point, does not act so well as light (experiments being made in sealed tubes to prevent loss of iodine)." With regard to this point, it is a mild criticism to make, that Dr. Smith could not have arranged the conditions of his experiment in a manner better calculated to lead him to conclusions utterly false: for, in sealing up the tubes, Dr. Smith prevented the access of oxygen, the very element whose presence is essential to the occurrence of the reaction with dilute solutions, whether the experiment be performed in light or darkness, in the heat or cold. And the sum total of the iodine which Dr. Smith could have liberated, under the conditions given, even had the tubes been kept at the boiling heat, or several degrees above (see results obtained at 105°, *supra*), for hours, would have been the small amount equivalent to the oxygen sealed up at the same time with the solutions in the tubes.

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very long sulphuric acid tube, and thence into an absorption apparatus containing *potassium iodide*, and provided with a proper sulphuric acid guard. In case the matter of ozone and oxygen were identical, the weight of oxygen equivalent to the weight of iodine set free by the ozone, should have been equivalent to the total gain in weight by the absorption apparatus. But, according to the experiments, this weight was less, and the numbers apparently assigned to electrolytic ozone the formula H_2O_3.

Three years later, the conclusions of Baumert were overthrown by Andrews, in his classic research upon the "Constitution and properties of ozone" (Phil. Trans., 1856, 1; Roy. Soc. Proc., **7**, 475; Ann. de Chim., **67**, 181; Journ. de Pharm., **30**, 3; Ann. der Chem. u. Pharm., **97**, 371; Pogg. Ann., **98**, 435). He demonstrated the fatal error in Baumert's experiments, in that the electrolytic ozone had contained a minute but determinable quantity of carbonic acid, which, unless exceeding precautions be taken, is always present in the evolved gas. Finding that the results obtained with a *neutral solution of potassium iodide*, varied irrationally and uncontrollably, Andrews in despair abandoned the use of the *neutral* and substituted a slightly *acidified* solution of potassium iodide. The free hydrochloric acid prevented the fixation of any traces of carbonic anhydride by the liberated base of the iodide, the anomalies disappeared, and by very numerous experiments, he succeeded in establishing that the weight of the substance which produced the decomposition (the active oxygen or ozone), was exactly equal to the weight of the iodine set free, and therefore no hydrogen, as well, could have been present.

The fact that the foregoing, which is the main truth, was thus triumphantly established by Andrews, has probably been the reason why the method he followed, of titrating ozone in an acidified solution of iodide, has been generally adopted and practised, even up to the present day, with, as we have previously seen, the commission of very serious error. For while Baumert failed in his reply (Pogg. Ann., **99**, 88) to invalidate the principal conclusion of Andrews, he nevertheless did succeed in experimentally proving that all of them were vitiated

It is possible that in the experiment performed by Dr. Smith, a small amount of the dilute nitric acid may have undergone resolution, by heating, into hyponitric acid and oxygen. But this is extremely improbable, and there is reason for believing that the total amount of iodine set free in the experiment cited, was the exact chemical equivalent of the oxygen of the air, which was sealed up at the same time with the acidified solution in the tube. And, as a corollary to this proposition, that, had Dr. Smith taken the precaution to exclude every trace of free oxygen from the tube, even with the dilute nitric acid, no change of the potassium iodide solution would have occurred on heating to the boiling point, and on continuing the heating for hours.

The 7th point is:—"The solution of iodide of potassium as hitherto obtained, is subject to change. An old solution, that is, one nearly a month old, was found more sensitive than a new one in all

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by a constant error. Baumert showed that when a stream of electrolytic ozone was passed through three absorption apparatuses, the first and second containing a neutral, the third an acidified solution of potassium iodide, all the ozone underwent decomposition in the first, no iodine whatsoever was liberated in the second, but in the third, *the acidified solution*, an amount of iodine was set free equivalent to many times (from 4 to 10) that corresponding to the ozone reaction in the neutral solution. This last, Baumert correctly ascribed to the decomposing action of oxygen upon an *acidified* solution of potassium iodide, and the curious fact remains that both the total increments in weight due to the fixation of absorbed ozone (and oxygen), and the amounts of oxygen as determined by titration equivalent to the iodine liberated, were both false in Andrews' experiments, and in excess of the absolute quantities of ozone operated upon. Yet, inasmuch as these two weights in the absence of an extraneous third body, like carbonic acid, which could be fixed by the titrating fluid, were necessarily equal, the constant error in Andrews' results did not excite general attention. Fortunately, as above remarked, the conclusions arrived at by Andrews were true, and the accompanying fallacy, concealed beneath the halo surrounding a great name, was perpetuated in the works of later experimenters, and has led many astray.

Ten years later than the memoir referred to, the facts made known by Baumert, concerning the decomposition of an acidified iodide solution in the presence of oxygen, were rediscovered by Payen (loc. cit.), who extended his trials to the action of acetic, nitric, oxalic, and other acids, in dilute condition, upon solutions of potassium iodide, in and out of contact with air, but without accompanying them with the beautifully quantitative methods of Baumert. While both experimenters noted the essential participation of oxygen in the change, they appeared to have overlooked the role of actinism.*

* Since writing the above, I have found (Chem. News, **36**, 100, from Gazz. Chim. Italiana, 7, Fas. 6) a note entitled, "Action of light and carbonic acid upon aqueous solutions of iodide of potassium, and on ozonoscopic paper, by G. Pellagri." I am unable to judge, from this short note, to what extent the above results have been anticipated by the Italian experimenter, and have no means of present access to the original paper.

cases tried." I find it difficult to understand the precise meaning of the epithet "sensitive," as applied in this connection, unless the sensitiveness be due to a decomposition of the nitric acid employed, and a corresponding liberation of iodine. In this case, however, instead of being styled sensitive, the solution might, with more propriety perhaps, be termed spoiled, and as such unfit for employment in actinometry.

Dr. Smith states in the ninth place:—"The amount of allowance to be made for temperature is not made out. It is not certain that any is required in the cases when weak acid is used. The weather has not allowed any combined action of great light and heat, but with heat and light in the rays from an electric light with a parabolic reflector, the action was very rapid."

I fail to find in the experiments detailed by Dr. Smith upon the effects of temperature (see above), a basis for the above generalization. Neither do I perceive the reason for this dependence upon the weather, when it might be deemed the essential prerequisite of accurate experiment, that the changes due to the two separate causes should be carefully discriminated, and the effects properly assignable to each, determined by previous trials under conditions admitting of exactitude and control. Nor do I recognize a test of the latter character, in the experiment performed in the concentrated beam from an electric light.

Finally, the manner in which the iodo-acid method is applied to solar actinometry, appears to me irrational. For Dr. Smith proposes to expose this actinometer during successive hours of "sunshine and cloud alternately"; during times when the weather is "changeable"; during intervals of "sun and showers"; during weather which is "foggy, with a gleam of sunshine." I am quite unable to understand in what way the value of a meteorological observation is enhanced, by knowing that, during periods in which the sun may or may not have been shining, a few milligrammes, more or less, of iodine were set free, in an acidified solution.

When, however, we call to mind the frequent experience in photography, that there are states of the atmosphere when, with a clear sky, the quality of the light does not appear to be favorable to the making of a successful picture; or the fact previously noted, that no visible change being manifest in a brilliant blue sky, the curve of chemical intensity underwent a great depression; or note the immense amount of chemical work done as the horizontal ray passes through the myriad organisms and pestilential germs, miasms,

vapors, and countless emanations from the earth's surface, that admit of oxidation under solar influence, then, I think, we become impressed with the large practical value of an easy and rapid method of actinometry. The actinic component of the solar ray has its units of work, as well as the thermal, and the day has come when, in the utilization of available energy, if it will not repay us to "extract sunbeams from cucumbers," it is because we can more profitably store up the wasted forces in the sun-beams ready made.

XXXI.—Laws governing the Decomposition of Equivalent Solutions of Iodides under the Influence of Actinism.

By Albert R. Leeds, Ph.D.

In a paper published in the *Philosophical Magazine* for June, 1879, I have given a brief review of the controversy as to whether potassium iodide, in very dilute solution, is decomposable by sulphuric acid. I likewise pointed out that the explanation of the opposite views entertained by experimenters upon this question, was due to their having overlooked the essential part played by air or oxygen in this reaction.

In former papers,* a summary of which is given in the *Philosophical Magazine* (loc. cit.), I have shown that the presence of oxygen not merely facilitates, but is absolutely essential to the occurrence of the reactions in all cases, and whether the reaction occurs in open or closed vessels, in the heat or cold, in darkness or in light. The only exception to this law is in the case of an acid like nitric acid, which under the influence of light (the action of heat alone in the absence of light and oxygen is being investigated) spontaneously breaks up, and supplies by internal change the essential oxygen. The experiments made to determine the rates of decomposition when various iodides in the presence of different acids, were submitted to the influence of the magnesium, electric and solar rays, were made with solutions of known, though not of chemically equivalent, strength. To supply this defect, a new series of experiments was performed immediately after the publication of those cited above, and it is to make known certain remarkable laws of actino-chemical change deduced from these later experiments, that the present article is written.

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* Compt. Rend., **62**, 254; Proceedings American Chemical Society, 1878, **2**, 4; Journal American Chemical Society, 1879, **1**, 18; ibid, 65.

The solutions were of such strength, that 1 c.c. of each of the acids employed was chemically equivalent to 12.6 c.c. of a normal caustic soda solution; the iodides were each exactly equivalent to the 20 per cent. solution of the potassium iodide; 1 c.c. of the iodide and 1 c.c. of the acid were used in each trial, the volume of the test being made up to 100 c.c. by the addition of distilled water. The tests were contained in comparison tubes made of thin, perfectly colorless glass, of uniform bore and dimensions, which were supported on frames in such a manner that each tube should be normal to the incident ray, and in the case of the magnesium and electric lamps, 6 in. from the focus of the light.

The first set of trials was made to determine whether the addition of starch as an indicator facilitated the decomposition under the influence of light, as had been originally supposed, or whether, as later on, there had been reason to think, it retarded the reaction. In this, as in succeeding experiments, the amounts of iodine liberated are given in milligrammes.

EFFECT OF STARCH UPON THE RATE OF CHANGE.

March 18th, 1879. (Brilliant Sun.)

Reagents	1.30—2.30 P.M. 5 c.c. starch-water	2.30—3.30 30 c.c. starch-water	3.30—4.30 No starch
H_2SO_4+KI	0.48	0.51	1.65
HCl + "	1.18	1.46	3.50
HNO_3+ "	3.10	2.57	3.50
H_2SO_4+CdI_2	0.49	0.82	1.65
HCl + "	1.90	1.11	3.55
HNO_3+ "	2.80	2.83	3.40
H_2SO_4+LiI	0.34	0.40	0.30
HCl + "	0.59	0.72	1.75
HNO_3+ "	2.70	3.86	2.75
H_2SO_4+KI	0.48	....	....
MARCH 19TH, 12 M.–1 P.M. (Feeble Sun-light.)			
H_2SO_4+KI	0.26	....	1.8
HCl + "	0.40	....	2.4
H_2SO_4+CdI_2	0.22	....	1.6
HCl + "	0.40	....	2.2
H_2SO_4+LiI	0.20	....	1.2

The experiments of March 18th, performed as they were with a sun approaching the horizon, having been less decisive than could have been desired, they were repeated upon the following day, but with the disadvantage of feeble sun-light, with the result of showing that six times more iodine was set free in the absence than in the presence of starch. The suspended precipitate of starch iodide cut off the light except upon the superficies of the solution. Henceforth the employment of starch was abandoned.

The next set of trials was instituted in order to observe the influence upon the rate of change, of larger access of oxygen than that derivable from the air already dissolved, or in contact with the solution at its upper surface. To this end tests were prepared in duplicate, and through one pair of these duplicate solutions, the comparison tubes being connected together in the manner of wash-bottles, a slow current of oxygen was passed.

INFLUENCE OF INCREASED SUPPLY OF OXYGEN,
March 19th, 1879. 11 A.M.–12 M. (Feeble sun-light.)

	With Oxygen.	Without.
H_2SO_4 + KI	7.15	2.9
HCl + "	10.60	4.3

Also with Nitric Acid. 1–2 P.M. (Snowing at time.)

	With Oxygen.	Without.
H_2SO_4 + KI	5.25	1.5
HNO_3 + "	6.75	2.5

Since 100 c.c. of water, when saturated with air under the ordinary circumstances of temperature and pressure, would hold in solution only about 1 mgrm of oxygen, the maximum amount of iodine which could be liberated during one of these tests, in case no fresh absorption of oxygen took place from the upper surface, would be 16 mgrms. The influence of these conditions upon the accuracy of the estimations made with the iodo-acid actinometers, is being submitted to further investigation.

In order to study the influence of mineral acids, trials were made as above, the solutions being of such strength that 1 c.c. of each was chemically equivalent to the same amount of the mineral acid.

EFFECT OF ORGANIC ACIDS, MARCH 20TH, 10.10 A.M.–1.10 P.M.
(Good sun-light.)

Oxalic	acid	+ potassium	iodide	= 6.50	mgrms I.
"	"	+ cadmium	"	= 6.00	" "
"	"	+ lithium	"	= 5.75	" "
Tartaric	acid	+ potassium	"	= 0.10	" "
"	"	+ cadmium	"	= 0.00	" "
"	"	+ lithium	"	= 0.00	" "

No change with acetic acid during this three hour interval.

To determine more precisely the rate of change effected by the organic, as compared with the mineral acids, it will be necessary to make simultaneous estimations, but even with oxalic acid, the most active of them all, it is evident that the amount of decomposition was relatively small.

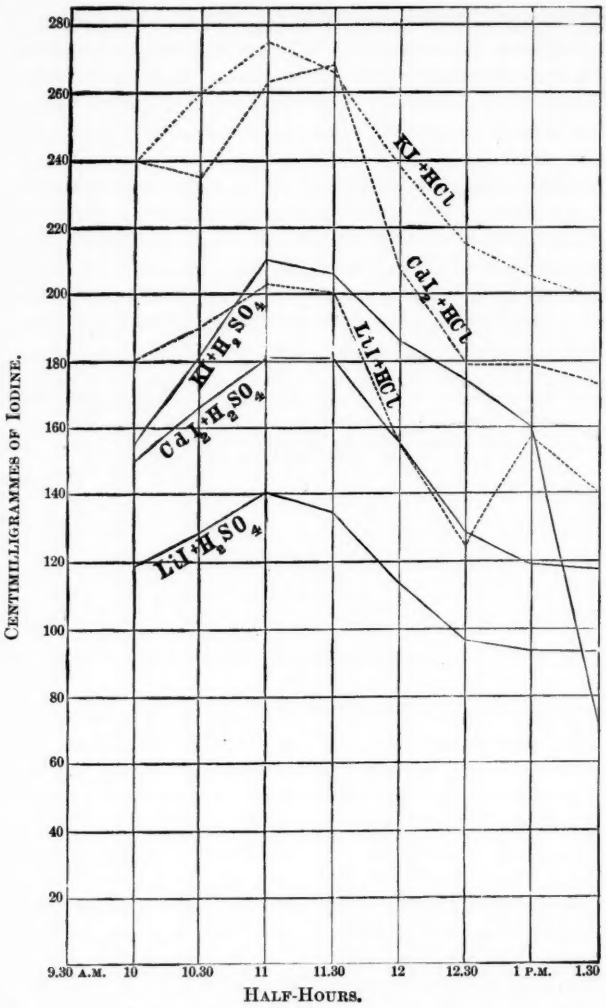
An actinometric measurement of the solar ray was made with the equivalent solutions of various iodides and acids, the principal object being to note the effect upon the rate of decomposition of different acids in the presence of the same base, and of different basic radicals of the iodides in the presence of the same acid. The sun-light, which was good during the early part of the day, declined towards noon, and shortly after the sky became overcast.

ACTINOMETRIC MEASUREMENT OF THE SOLAR RAY, MARCH 26TH, 1879.

	9.30–10 A.M	10–10.30	10.30–11	11–11.30	11.30–12 M.	12 M.–12.30	12.30–1 P.M	1–1.30	MEANS	RATIOS.
H_2SO_4 + KI	155	181	21	206	187	17	16	75	168	H_2SO_4 : HCl
HCl + "	24	26	275	266	239	215	205	20	250	1 : 148
H_2SO_4 + CdI_2	15	162	181	181	156	129	119	118	149	H_2SO_4 : HCl
HCl + "	24	235	263	268	209	179	179	175	218	1 : 146
H_2SO_4 + LiI	118	128	141	135	113	96	93	93	115	H_2SO_4 : HCl
HCl + "	183	19	203	20	156	125	158	14	169	1 : 147

These results are represented graphically on the diagram on the following page.

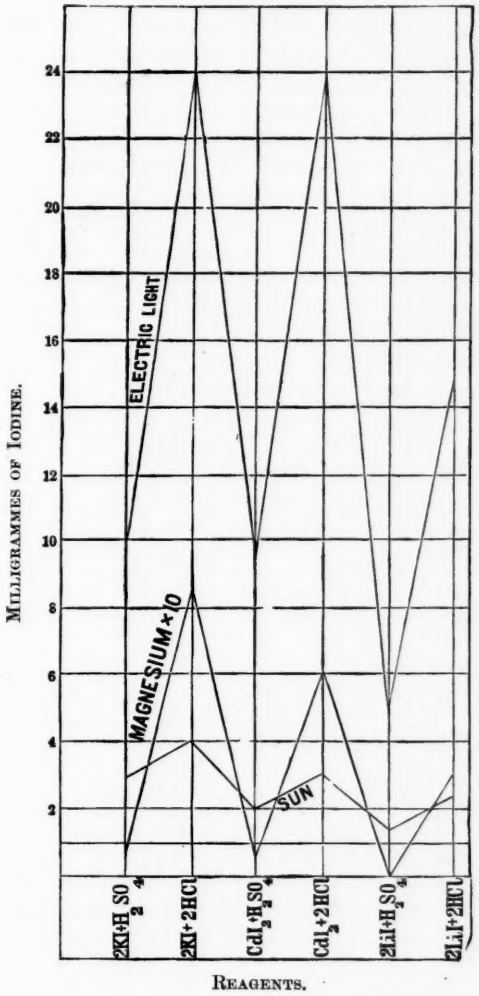
On comparison of the arithmetical means of the results obtained in 54 trials made during the course of the same day, the striking fact is brought out, that the amounts of iodine liberated by the two acids in the presence of the same base, stand in a constant ratio to one another. The law of actinic force herein indicated may provisionally be expressed by the formula—the chemism of the chlorine radical is to that of the $\frac{1}{2}SO_4$ radical (measured by the relative amounts of iodine liberated by each respectively, in solutions of the metallic iodides exposed to sun-light) as 1.47 : 1. There is reason for inferring from the experiments, that a similar definite ratio exists between the amounts of iodine liberated from different soluble iodides in the presence of the same acid.



COMPARISON OF THE ACTINIC INTENSITIES OF THE SOLAR, ELECTRIC AND MAGNESIUM LIGHT.

In making this comparison, the amounts of iodine liberated at the hour of maximum actinic intensity (1–1.30 P.M.) were taken in the case of the sun. The electric light was that emanating from a lamp of 7000 candle power, falling upon the solutions at a distance of six

inches; the magnesium light, that derived from the burning of a single ribbon in the ordinary lamp, placed at the same distance. The time of exposure to the electric light was 10 minutes; to the magnesium light, 25 minutes; to the sun, one-half hour; in the table, all are calculated to one hour.



	Solar.	Electric.	Magnesium.
$H_2SO_4 + KI$	2.70	10.0	0.084
HCl + "	4.00	24.0	0.870
$H_2SO_4 + CdI_2$	2.04	9.5	0.072
HCl + "	3.00	24.0	0.600
$H_2SO_4 + LiI$	1.44	5.0	none
HCl + "	2.40	15.0	0.300

On examining this table, and still more readily the graphic illustration preceding it, two phenomena become forcibly manifest:—1st. The very much greater actinic intensity of the electric, as compared with the solar ray, when compared in the manner indicated, and the very much less intensity of the magnesium. In order to bring the magnesium curve into the same diagram as the others, the numbers in the magnesium column in the table were all multiplied by ten. 2d. Instead of the relative chemism of the chlorine atom, as estimated by its iodine-liberating power under these conditions, being 1.5 in all three cases, it is 6 with the electric, and 10 with the magnesium light. The examination of these differences, as related to the actinic forces of different sources of light, and to different acid and basic radicals, is being investigated further.

Finally, the influence of absorbing media upon the invisible rays of the sun and electric light were determined, the comparison tubes being surrounded with a thickness of 3 c.m. of ammonio-sulphate of copper, neutral potassium chromate and fuchsine, each solution being brought to the same apparent degree of translucency, for the blue, yellow, and red respectively. The exposure to the sun was from 9.30 A.M. to 5.30 P.M.; to the electric light, 20 minutes; but both are reduced to the interval of 1 hour.

		Sun.	Electric Light.
Blue	$H_2SO_4 + KI$	0.74	1.800
	HCl + "	1.12	6.750
Yellow	$H_2SO_4 + KI$	0.11	0.000
	HCl + "	0.25	0.125
Red	$H_2SO_4 + KI$	0.28	0.600
	HCl + "	0.56	2.250

These figures show that the selective action of absorbing media upon the invisible rays of different illuminants, varies greatly; and suggests the employment of this method for the mapping out of absorption spectra for the actinic portion.

XXXII.—On the Action of Hyponitric Anhydride on Organic Bodies.

By ALBERT R. LEEDS, Ph.D.

I.—ACTION UPON BENZINE.

The author was led to an extended study of the action of hyponitric anhydride upon organic bodies, by certain theoretical considerations as to the nature of the derivatives which could possibly be obtained by the operation of this powerfully oxidizing anhydrous radical upon benzine. The results having exceeded in number and importance the most sanguine expectations entertained at the outset, the investigation has been extended to a large number of bodies in the aromatic group, and in the future will be made to include as many organic substances, as will be likely to undergo change when submitted to this reagent. So far as we have been able to discover, but few investigators have turned their attention in this direction. Guthrie found that when hyponitric anhydride is passed into a flask containing amylene and surrounded by a freezing mixture, the gas is instantly absorbed, and the amylene is gradually converted into a pasty mass of minute crystals, which may be purified by washing with cold alcohol, recrystallization from boiling ether, and drying in vacuo over sulphuric acid. Its analysis gave the formula $C_5H_{10}(NO_2)_2$, which would make it a direct combination of the monatomic radical nitrile with the radical amylene, a *nitrilide of amylene*.*

According to Semenoff,† when dry ethylene gas is passed through liquified hyponitric anhydride, or when the mixture of the two gases is heated to 60° or 70°, ethylene nitrite, $C_2H_4(NO_2)_2$, is formed, together with an oily body. It may be obtained in a pure condition and more abundantly, by passing ethylene into anhydrous ether, liquid hyponitric anhydride being added at the same time, drop by drop, and, after the liquid has cooled, drying the crystals, which separate, between filter paper and finally over sulphuric acid. It is insoluble in water, easily soluble in alcohol and ether, and crystallizes in four-sided tables, melting at 37.5°.

Finally it is stated,‡ that certain nitro-derivatives have been formed by the direct action of hyponitric anhydride upon organic bodies, *e. g.*, mononitronaphthalene, $C_{10}H_7(NO_2)$. But more explicit

* Quar. Journ. Chem. Soc., **13**, 45, 129.

† Zeitschr. Chem. Pharm., 1864, 129.

‡ Dictionary of Chemistry, Watts, **4**, 77.

references to the reactions alluded to, we have not succeeded in finding.

In the first experiments, benzine was treated with nitric oxide, to determine whether this body would exert an action upon it, and when negative results were obtained, dry hyponitric anhydride was used. The absorption, both in the cold and in boiling benzine, is energetic, the liquid becoming of a deep red color, and the increase in volume, in the case of cold benzine, very striking. At the beginning, before many unsuccessful experiments had acquainted us with the method of obtaining more satisfactory results, the mistake was made of subjecting the benzine, thus hyponitrified in the cold, to distillation. Large volumes of hyponitric anhydride were given off, and a brownish-red viscid mass remained behind. In some of the earlier experiments this residue was found to contain nitrobenzine, in other trials, none. A portion, free from nitrobenzine, was treated with caustic potash, with which it readily combines, and precipitated again with hydrochloric acid. This operation was repeated several times, but without obtaining a body capable of crystallizing from any solvent. Finally, the original residues were dissolved in ether, and the concentrated etherial solutions washed repeatedly with water. The viscid mass, left on evaporation of the ether, solidified into a translucent, dark red substance. This, on analysis, gave a formula corresponding to $C_6H_6(NO_2)_2(OH)_2$.

	FOUND.		THEORY.
	I.	II.	
Carbon	34.7 per cent.	34.2 per cent.	35.3 per cent.
Hydrogen	3.2 "	4.2 "	3.9 "
Nitrogen	....	14.0 "	13.7 "

The extreme improbability of having formed a substance with this constitution, and the failure to have obtained it in a crystalline condition, made it well-nigh certain that the body analyzed was a mixture. The method of preparation was therefore entirely changed. The benzine, contained in a series of wash-bottles surrounded by cold water, was treated with a slow stream of hyponitric anhydride for many days, until it ceased to increase in volume or weight. The product was set aside for several weeks, the bottles being loosely plugged with cotton-wool. The excess of uncombined gas passed off, and the liquid separated into two layers, both of a yellow color, but the lower of an oily character and consisting of nearly pure mononitrobenzine.

To determine what was the nature of the gases evolved during nitration, they were passed into a jar over alcohol, in order to dissolve

any escaping benzine, and after standing for some time, were examined for oxygen, nitric oxide, etc. It was found that they consisted mainly, if not entirely, of nitrous oxide, N_2O. No nitric oxide was detected, and this very interesting result makes strikingly evident the energy of hyponitric anhydride as an oxidizing agent for organic substances.

On distilling the liquids, the temperature finally rose to 209°, after the unaltered benzine had gone off, and the oil of bitter almonds distilled over. Surrounded by a freezing mixture, it solidified into a mass of long colorless, prismatic crystals, proving that the oil was pure mononitrobenzine, $C_6H_5(NO_2)$. Prior to distillation, the liquids deposited crystals, which were either white, or stained to a greater or less extent by adhering drops of a dark red oil. A great deal of time was wasted in endeavoring to purify these crystals by crystallizing them from various solvents, benzine, acetic acid, alcohol and ether, in the last-named of which they dissolve easily. But, unfortunately, the result proved that the same source of error was present here, as when the original product of hyponitrification was dissolved in ether—the crystals were never entirely free from a foreign body likewise soluble in ether. An analysis of the crystals obtained by recrystallization from this solvent, afforded: carbon, 22.03 per cent., hydrogen, 4.22; corresponding to the formula, $C_6H_{14}O_{15}$. The melting point of the crystals was 99°, beyond which point they were decomposed with evolution of water and deposition of fine needles.

The above, very improbable, formula led to the abandonment of the methods of purification heretofore employed, and the substitution of an entirely different one. The crystals were dissolved in water, in which they were readily soluble, and their lead and silver salts precipitated by plumbic acetate and argentic nitrate. Both salts were entirely insoluble in water, the lead salt, after repeated treatment with hot water, remaining of a fawn yellow color.

0.689 grm of the lead salt yielded 0.6806 grm $PbSO_4$, or 67.4 per cent. of lead to 32.6 per cent. of the organic radical. This would require that the equivalent obtained for the organic radical should be multiplied by three, in order to make it correspond with the equivalent of $C_6H_{14}O_{15}$.

1.0941 grm of the silver salt yielded 1.0065 grm AgCl, or 69.2 per cent. of silver to 30.8 per cent. of the organic radical. Hence, the number found for the latter had to be multiplied by six, in order to make it correspond with the equivalent of $C_6H_{14}O_{15}$.

Some of the crystals obtained from this acid body by sublimation, as detailed above, were dissolved in water, and an analysis made of the lead salt precipitated from this solution. 0.3568 grm of the salt yielded 0.3496 grm $PbSO_4$, or 66.8 per cent. of lead to 33.2 per cent. of the organic radical. This salt was evidently identical with that obtained from the hydrated acid in the first instance, and the equivalent deduced from the analysis had to be multiplied by three, in order that it should correspond with the equivalent of $C_6H_{14}O_{15}$.

These results made it appear eminently probable that the body was $3(C_2H_2O_4).2H_2O$, or, in other words, that the empirical formula, $C_6H_{14}O_{15}$, corresponded to three molecules of oxalic anhydride plus two molecules of water, the excess in hydrogen being due to a slight admixture of a foreign body. That the acid substance produced by the oxidation of benzine with hyponitric anhydride was oxalic acid, had been long suspected, but the lack of exact correspondence in properties, as for instance, the obtaining of a slightly colored lead salt, the somewhat explosive nature of the silver salt, etc., had demanded a more satisfactory verification.

To this end, a number of apparently pure crystals were picked out of the deposit on the sides and bottom of the nitrobenzene mother liquor, and after careful drying between filter paper, and recrystallization from alcohol, were placed in a desiccator over sulphuric acid. In their original condition they were perfectly colorless, like glass, and melted at 99° with disengagement of water; after desiccation, the same crystals were entirely white, non-transparent, melted at 185°, yielded no water, but, before melting, partly sublimed in the form of prismatic needles.

0.316 grm of the desiccated crystals, yielded, on analysis, 28.22 per cent. of carbon, and 1.89 per cent. of hydrogen, corresponding to the formula $C_6H_4O_{11}$.

Another portion of the crystals, picked out and freed from all adherent foreign matter with exceeding care, was recrystallized from acetic acid, and a weighed portion of the product thus obtained was subjected to desiccation over sulphuric acid, and, after complete drying, to analysis—0.4518 grm of the acid, after desiccation, had diminished to 0.3213 grm, a loss of 28.88 per cent.

0.2894 grm of the anhydrous body, yielded 0.2840 grm carbonic anhydride and 0.068 grm water.

	FOUND.	THEORETICAL.
Carbon	26.76 per cent.	26.66 per cent
Hydrogen	2.61 " "	2.22 " "
Oxygen	....	71.11 " "

Or the anhydride had the composition, $C_2H_2O_4$, and the water percentage corresponded to two molecules H_2O, proving that the crystalline substance was no other than $C_2H_2O_4,2H_2O$, oxalic acid.

The experience thus obtained made the separation of the other products of nitration comparatively easy. After all the excess of hyponitric anhydride had passed off, and the crystals of oxalic acid had separated out, the liquid portion was boiled with a large excess of water; this drove off the unaltered benzine and the mononitrobenzine. On filtering the intensely yellow colored solutions thus obtained, and concentrating the filtrates, a large mass of fern-shaped, yellow crystals separated out. On washing and drying, their melting point was found to be 118°, and instead of washing the entire mass with water alone, a mixture of hydrochloric acid and water was used, the crystals being less soluble in the acidulated liquid. Of the various solvents employed in recrystallizing the impure substance melting at 118°, such as alcohol, acetic acid and chloroform, the last was found to afford the best results. The final crystallization from chloroform was in brilliant prisms, one and one-half c.m. in length, apparently trimetric, doubly terminated by the faces of the unit octahedron, and exhibiting the vertical and macrodiagonal prisms. Though the melting point could not be raised by recrystallization higher than 122°, and the crystals were not entirely colorless, yet the attempt to deprive them entirely of their yellow tint, by repeated crystallization, was unsuccessful. The solution of these crystals in water was a golden yellow, staining the skin intensely, and permanently dyeing wool and silk. Its taste was extremely bitter. These properties, its crystalline form, the presence of nitrogen, and melting point, all rendered it highly probable that the substance was trinitrophenol or picric acid, $C_6H_3(NO_2)_3OH$; a supposition which was confirmed by the analysis:

	FOUND.	THEORETICAL.
Carbon	31.51 per cent.	31.44 per cent.
Hydrogen	1.76 " "	1.31 " "
Nitrogen	.... " "	18.34 " "
Oxygen	.... " "	48.91 " "

After the various extracts with water, ceased to deposit crystals, they were evaporated to dryness on the water-bath. The reddish-yellow crystalline mass thus obtained, was found to consist of oxalic acid, picric acid, a small amount of the non-identified reddish coloring matter, and a quantity, likewise small, of a substance exploding with violence when heated. This last body was too minute in amount to isolate, but was supposed to be a compound of picric acid with the mono- or one of the dinitro-derivatives of benzine.

It has previously been mentioned that the best results were obtained when a slow current of hyponitric anhydride was passed through a series of wash-bottles containing benzine, and surrounded with cold water. In this case, after standing for several weeks, large colorless crystals of oxalic acid separated out, which might be purified from foreign matters most effectually by crystallization from their solution in acetic acid. It has also been mentioned, that when these crystals were formed in benzine, which had been hyponitrified at higher temperatures, they were accompanied by a deep red oil, from which they were purified with extreme difficulty. Still more was this the case, when the hyponitric anhydride was passed over benzine, which was heated on a water-bath, and provided with an apparatus for condensing vapors.

In one instance, however, there was a *mass of yellow crystals found in the bottle containing the distillate.* This consisted of two entirely different bodies; the one, soluble in alcohol more especially when boiling, and from which it was finally obtained on the third recrystallization, as slender prismatic needles, not exceeding a few millimeters in length, and of a faint reddish-yellow color. On heating, it does not melt, but at 215° begins to sublime, and deposits light yellow, prismatic needles, which, though extremely fine, are, in the case of some crystals, as much as a centimeter in length.

The other substance is insoluble in alcohol, but soluble in benzine, from which it crystallizes in brilliant lemon yellow prisms. These prisms exhibit vertical prismatic faces, with lateral replacements, and are twinned in columnar aggregates. Unlike the crystals soluble in alcohol, which polarize magnificently, those obtained from benzine do not polarize, neither do they melt, but sublime at a point a few degrees higher than the other substance, or, as near as could be ascertained, at 220°.

0.3207 grm of the crystals soluble in alcohol, yielded 0.923 grm CO_2 and 0.1152 grm water, corresponding to the formula, C_6H_4O. Repeated trials showed the entire absence of nitrogen.

	FOUND.	THEORETICAL.
Carbon	78.49 per cent.	78.26 per cent.
Hydrogen	3.86 " "	4.35 " "
Oxygen	.... " "	17.39 " "

Whilst the formation of quinone might not unreasonably be anticipated, yet it is evident that the new substance which we have obtained, differs strikingly not only in composition but in physical characters, from quinone. For while the latter crystallizes in golden

yellow prisms, it melts at 116°, and even at common temperatures sublimes in shining needles. Moreover, its odor is so pungent as to excite tears, while the new substance is entirely odorless. For the lack of a better name, I shall provisionally call this new oxygen derivative of benzine, monoxybenzine.

The other body, the one soluble in benzine, I did not obtain in quantity sufficient for analysis. Very many attempts were made, the details of the experiments being varied in every way which promised favorable results, but without success. It is hardly necessary to say that the failure to obtain a second time, so important a new substance as the monoxybenzine, and the accompanying body as well, was utterly inexplicable, and the inability to devise any new explanation of the failures, or any different method of work, must be my apology for making known at this stage in the investigation, what was actually accomplished in the first, and by accident apparently, the only successful experiment.

II. ACTION UPON NAPHTHALENE.

In the first experiment, 120 grms of naphthalene were treated in the cold with hyponitric anhydride, until the weight had increased to 199 grms. The naphthalene at first became liquid and of reddish color, and then began to deposit needle-shaped crystals. The resulting product was first distilled with water, in order to get rid of any naphthalene not acted upon, and the residue distilled off at a temperature of 303°. The distillate, which was a yellowish-white solid mixed with some oily matter, was recrystallized a number of times from alcohol, until it yielded nearly white, prismatic needles, having a melting point of 60°, and was thus shown to be nitronaphthalene, $C_{10}H_7(NO_2)$.

As there were evidently other substances formed, besides the nitronaphthalene, it was thought possible that by the action of reducing agents some of these might undergo reduction and others not, and in this way a method of separation be arrived at. After reduction by tin and hydrochloric acid, and separation of the dissolved tin, a clear reddish solution was obtained, from which, on the addition of ammonia, a greenish precipitate was thrown down. This dissolved in alcohol to a red liquid, which exhibited a beautiful blue fluorescence. A portion of the original nitrated mass did not appear to undergo reduction. It dissolved readily in alcohol, but did not crystallize from this or any other solvent. Its solution was of a red color, but not fluorescent. Later on, it was found that the fluorescent body was contained in the first portion of the greenish precipitate, with

ammonia. Moreover, it was found that it was less soluble in hydrochloric acid than the naphthylamine, with which it was associated. After treating the precipitate a number of times with hydrochloric acid, and reprecipitating with ammonia, a substance was obtained which fluoresced very strongly, but which failed to crystallize from any solvent employed. This mode of separation was therefore abandoned.

In the third trial, 150 grms of naphthalene increased in weight to 270 grms, and after first becoming liquid, on the continued passage of the gas, again solidified. After twice distilling with water, the residue was repeatedly treated with cold alcohol. The portion remaining was then dissolved in hot alcohol, from which it separated in colorless, prismatic needles, subliming without decomposition. By their containing nitrogen and by their melting point, these were proven to be α-dinitronaphthalene, $C_{10}H_6(NO_2)_2$.

Finding that ligroine did not dissolve the red coloring matters, while it did dissolve the nitro-derivatives, a portion of the nitrated mass was treated four times with this solvent raised to the boiling point. The residue was then repeatedly treated with cold alcohol, which dissolved out the coloring matter, and from the undissolved portion was obtained β-dinitronaphthalene.

An attempt was then made to isolate the bodies accompanying the nitro-derivatives, by treating the original mass with potash. On boiling, this effected a nearly complete solution, and after filtration the solution was treated with excess of hydrochloric acid. The filtrate was then exhausted with ether. This operation was repeated a number of times, until a considerable quantity of a red viscid mass was obtained on evaporating the etherial extract. This was again subjected to the same process as before, until a dark red, and apparently, a homogeneous non-crystalline substance, was obtained. Further examination, however, proved that this was not the case, the dark red oil accompanying the nitro-derivatives, effecting a partial solution of these bodies when the mass was treated with potash, and causing them to pass to a certain extent into the final product. This process was therefore abandoned.

280 grms of the naphthalene, heated upon a water-bath, in a retort provided with a wide condensing apparatus, were now hyponitrified. The action was very energetic, streams of oil running down the sides of the retort, and the condensing chamber becoming covered with long white crystals of nitronaphthalene. The final product, which solidified on cooling, was distilled, the temperature rising as the mass

darkened, from 213° to 320°, and the distillate being collected in several portions. The first portions, after repeated crystallizations from alcohol, yielded nitronaphthalene, with a melting point of 59–60°. But neither benzine, ether, alcohol, chloroform, acetic acid or ligroine, were able to extract from the distillates or from the original product, any other substances than the mono- and dinitro-derivatives, the associated red coloring matter resisting all attempts to obtain it in a state of purity.

Another portion of naphthalene, nitrated while hot, was repeatedly boiled with water. On cooling, the solutions were filtered and evaporated, until a thick mud-like sediment had settled. It weighed on drying 33 grms; the naphthalene from which it was obtained weighed 300 grms, and had increased on nitrating to 450 grms. The dried aqueous extract was placed in a retort, and the temperature raised to 215°, at and somewhat below which point, white opaque needles were sublimed off, with a melting point of 127°. Afterwards a white crystalline mass came over. On resubliming the crystals first obtained, long flat, pearly needles were formed, with a melting point of 131°. These polarized finely, while the former did not, a result attributed to some impurity. Later on it was found, what at the time was not anticipated, that this sublimate consisted of two white crystalline substances.

Analyses of the sublimate (melting point, 131°):

	I.	II.	III.	IV.
Carbon	65.44 per ct.	51.14 per ct.	66.40 per ct.	66.07 per ct.
Hydrogen	2.75 "	2.78 "	1.96 "	2.44 "
Oxygen (by diff.)	31.81 "	46.08 "	31.64 "	31.49 "

Corresponding to the formulae, (I) $C_{11}H_5O_4$, (II) $C_{10}H_5O_7$, (III) $C_{11}H_4O_4$, (IV) $C_{11}H_5O_4$.

These irrational formulae manifested the probable impurity of the substance, and search was made to find appropriate solvent. It was insoluble in water, slightly soluble in chloroform, easily soluble in acetic acid, ether, alcohol and benzine. *The entire sublimate* (see above) was therefore dissolved in hot benzine. On cooling, minute fern-like crystals separated out, and then, after a long interval, and considerable evaporation, another crop of crystals, entirely different in form and appearance from the preceding, was obtained. The latter, on slow recrystallization from benzine, formed large prisms, apparently monoclinic, perfectly colorless, and of a high vitreous lustre. Another crop of this substance formed twin crystals, some of them of great size, one weighing 0.3 grm and being 42 m.m. long,

7 m.m. wide and 1 m.m. thick. The melting point was 131°. The other substance, far less soluble in benzine, had a melting point of 225°. The analysis of the latter was as follows: 0.153 grm of the substance yielded 0.5301 grm CO_2 and 4.16 grm H_2O, corresponding to the formula, $C_{10}H_8O_4$.

	THEORETICAL.	FOUND.
Carbon	62.50 per cent.	62.40 per cent.
Hydrogen	4.16 "	4.16 "
Oxygen	33.34 "	33.44 "

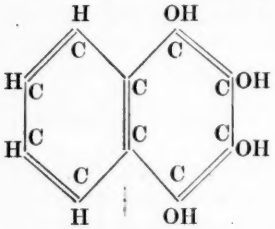
A number of analyses of the substance, with melting point, 131°, were made, with the following results:

(1) 0.3812 grm yielded 0.8961 grm CO_2 and 0.1601 grm H_2O.
(2) 0.2327 " " 0.5569 " " " 0.0602 " "
(3) 0.2793 " " 0.6580 " " " 0.0736 " "
(4) 0.2049 " " 0.4804 " " " 0.0540 " "

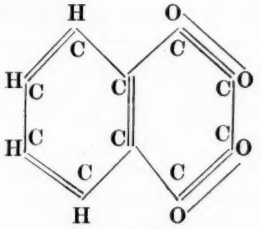
The formula deduced from the above is $C_{10}H_4O_4$.

	(1)	(2)	(3)	(4)	THEORETICAL.
Carbon	64.04	63.98	64.29	63.94	63.83
Hydrogen	2.91	2.87	2.89	2.43	2.13
Oxygen	31.05	33.15	32.82	33.63	34.04

The substance $C_{10}H_8O_4$ would therefore be tetroxynaphthalene, the substance $C_{10}H_4O_4$, naphthodiquinone, and the structural formulae of the two bodies might be represented by:



Tetroxynaphthalene.



Naphthodiquinone.

The discussion of the derivatives obtained from these extremely interesting new bodies, and of their theoretical relationships, will be left to a subsequent paper.

III. ACTION UPON CYMENE.

240 grms of cymene were treated in the cold, with hyponitric anhydride for a number of days. Unfortunately, the total increment in weight was lost, but eventually the cymene, after the operation

had been interrupted, and the excess of gas had been allowed to diffuse off, was found to have been converted into a very viscid dense liquid, of a light yellow color. This was repeatedly boiled with large quantities of water, until no more went into solution, the yellow liquid thus obtained depositing abundant crops of light yellow crystals on cooling. By repeated crystallization from boiling water, these crystals became perfectly white. They melted at 178°, afterwards subliming in thick needle-shaped crystals, and proved to be paratoluic acid, $C_8H_8O_2$.

In the first portions of the distillate, obtained when the raw product was being boiled with water, a small amount of a light yellow oil came over, which differed very slightly in specific gravity from the water condensed at the same time. It was purified by repeated washing with boiling water. Owing to the small quantity obtained, its specific gravity was determined with difficulty, the number found being 1.05. A qualitative analysis showed the presence of nitrogen, and the oil was therefore assumed to be α-nitrocymene, the specific gravity of which is stated to be 1.03.

The residue, after the extraction of the paratoluic acid and α-nitrocymene, was a viscid red mass, which resisted all attempts to crystallize or sublime, and was therefore set aside.

The yellow solutions from which the paratoluic acid had crystallized out, were evaporated to dryness, with the result of obtaining merely residual traces of paratoluic acid, and some of the red viscid body (probably containing a dinitro-derivative) above mentioned.

A large number of other substances, toluene, xylene, phenol, aniline, etc., are being treated with the hyponitric anhydride, and in a subsequent communication I hope to set forth the very interesting results which are being obtained.

In conclusion, I desire to acknowledge with great pleasure the aid rendered by my friend and assistant, Dr. Edgar Everhart, throughout this long and somewhat laborious research.

Abstracts from American and Foreign Journals.

Journal fuer Praktische Chemie.

Abstractor, EDGAR EVERHART, Ph.D.

On the Ethylsulphates of the Poly-Acid Alcohols and the Carbohydrates, with some Remarks on the Constitution of the latter, P. CLAESSON (**20**, 11).—Chlorsulphuric acid, SO_3HCl, was allowed to act on the polyatomic alcohols, by adding the latter gradually to the acid, which was kept at a low temperature. The aqueous solution of the saturated ethylsulphates is decomposed at first rapidly, afterwards slowly, into sulphuric acid and ethylsulphates of a lower degree of saturation; on warming, however, they are decomposed into sulphuric acid and alcohol. The salts of the ethylsulphates are either amorphous and very soluble, or crystalline and soluble with difficulty, or insoluble.

Glycoldisulphuric acid is a thick liquid insoluble in ether. It is decomposed at 150°. The barium salt, $C_2H_4(SO_4)Ba + 2H_2O$, crystallizes in hair-like needles. The potash salt is anhydrous, and forms a silver-like crystalline mass. The other salts are amorphous.

Glycerinetrisulphuric acid is a snow-like crystalline mass. It is very deliquescent, and on contact with water evolves much heat, with a partial decomposition into acids of a lower grade of saturation. All its salts are amorphous. When the acid, itself, is mixed with ice-cold water, and allowed to stand for a day, it is decomposed, yielding glycerinedisulphuric acid.

Erythritetetrasulphuric acid is also a snow-white crystalline mass, of small prismatic crystals. By long warming on the water-bath with an excess of water, it is reconverted into erythrite. The potash salt, $(KOSO_2O)_4C_4H_6 + 4H_2O$, crystallizes in six sided tables. It is very slightly soluble in cold water, but more easily in hot. The barium salt, obtained by the double decomposition of the potash salt, forms prismatic crystals that are insoluble in water and acids.

Mannitehexasulphuric acid could not be obtained in a pure condition. When the aqueous solution of the acid is neutralized with barium carbonate and, after filtration, mixed with absolute alcohol, the barium salt separates as an oil, which crystallizes spontaneously and then becomes perfectly insoluble in water and acids. Its composition is $C_6H_8(SO_4)_6Ba_3 + 5H_2O$. At 100° it becomes black, and is decomposed. The other salts are amorphous and easily soluble. The free acid and its salts rotate polarized light to the right. If the aqueous

solution is allowed to stand for forty-eight hours, it is decomposed into mannitetetrasulphuric acid. A longer standing produces a further decomposition.

Dulcite dissolves in SO_3HCl with the formation of dulcitane, which in turn yields dulcitanepentasulphuric acid. This acid could not be obtained pure, and its barium salt forms a hygroscopic amorphous powder.

Grape sugar, dextrine, starch and cellulose, dissolve in chlorsulphuric acid, and form one and the same crystalline compound, dextrosemonochloridetetrasulphuric acid, $C_6H_3O(SO_4H)_4Cl$, which rotates the plane of polarization strongly to the right, is deliquescent, and is easily decomposed by water, yielding a salt free from chlorine. The aqueous solution of the acid, after standing a day, is changed into dextrosetrisulphuric acid.

Inuline acts very energetically on chlorsulphuric acid, and seems to form a like levulosesulphuric acid, but owing to the ease with which it is decomposed, it could not be prepared.

Cane sugar is split up into dextrose and levulose by the action of SO_3HCl. Milk sugar yields a crystalline compound corresponding to dextrosechloridetetrasulphuric acid.

On the Presence of Bacteria, or their Germs, in the Organs of Healthy, Living Animals, M. Nencki and P. Giacosa (**20**, 34).—The authors describe a number of experiments in which they recognized such presence.

Results of the Norwegian North Sea Expedition, H. Tornöe (**20**, 44).—The author has estimated the amount of carbonic acid at different depths and in different degrees of latitude, without finding, however, any law governing the amount of acid. The neutral-combined carbonic acid varied from 51.4 to 55.4 mgrms per liter, and the acid-combined, from 39.7 to 47.9 mgrms per liter.

On the Recovery of Sulphur from Sulphurous Acid and Sulphuretted Hydrogen, J. Stingl and Th. Morawski (**20**, 76).—The authors investigated the method of Schaffner and Helbig for the recovery of sulphur and carbonate of lime from soda residues. This method consists in treating the fresh soda residues with a corresponding amount of magnesium chloride, in hermetically closed iron retorts, at an elevated temperature, whereby magnesium hydrate and sulphuretted hydrogen are obtained:

$$CaS + MgCl_2 + 2H_2O = CaCl_2 + Mg(OH)_2 + H_2S.$$

The sulphuretted hydrogen then coming in contact with sulphurous acid and a solution of magnesium or calcium chloride, deposits sul-

phur in a flocky, quickly subsiding precipitate. The same solution of $CaCl_2$ or $MgCl_2$ may be used repeatedly. Stingl and Morawski have found, that according to the concentration at a higher or lower temperature, the magnesium chloride and calcium sulphide react on each other, producing a magnesium sulphide, probably Mg_4S_5, which, in turn, at an elevated temperature in contact with water, is resolved into $Mg(OH)_2$, with the formation of H_2S.

In the action of sulphuretted hydrogen on sulphurous acid, sulphur and pentathionic acid are formed, the yield of sulphur being largest when the H_2S is in excess, and the solution of sulphurous acid is very dilute. Pentathionic acid, the authors state, is decomposed by the carbonates of the alkalies and the alkaline earths, in the cold, to tetrathionic acid, but in the heat, to tetrathionic acid and sulphur. The sulphur precipitated in these reactions quickly settles in flakes when a salt is present.

Contribution to the Chemistry of the Chrom-Ammonia Compounds, S. M. JÖRGENSEN (**20**, 105).—The author begins with chloropurpureochromium chloride, which is best prepared by allowing the chromium chloride to oxidize in an ammoniacal solution of ammonium chloride, and by precipitating the same by boiling with hydrochloric acid. At the same time, minute traces of luteochromium chloride are formed. The chloropurpureochromium chloride, $(Cl_2[Cr_2 10NH_3])Cl_4$, precipitated by hydrochloric acid, forms red, anhydrous, microscopic, octahedral crystals, that are soluble with difficulty in cold water. The neutral aqueous solution is very unstable, light quickly decomposing it with the separation of hydrated oxide of chromium. Boiling the aqueous solution changes it partly into the roseochromium chloride. The ammoniacal solution, on boiling slowly, deposits hydrated oxide of chromium; the presence of ammonium chloride, however, prevents the decomposition. The alkaline solutions of the salt are violet colored. In acids the chloropurpureochromium chloride is insoluble; in fact, the acids precipitate it from its salts. Nitrate of silver precipitates only 4Cl, the other two atoms are only precipitated on boiling. In this respect it behaves exactly like the corresponding cobalt compound.

The author goes on to describe the action of various substances, such as KCN, K_2CrO_4, $Na_2S_2O_3$, $K_2Cr_2O_2$, H_2S, &c., on the chromium salt.

The platinum double salt, $Cl_2[Cr_2 10NH_3](PtCl_6)_2$, is a brown, crystalline precipitate. The other salts, which correspond to the general formula $(Cl_2[Cr_2 10NH_3])R_4$, are obtained by adding the

aqueous solution of chloropurpureochromium chloride (prepared in the cold) to the necessary acid. The bromide, $(Cl_2[Cr_2 10NH_3])Br_4$, forms carmine red needles; the mercury double salt, $Cl_2[Cr_2 10NH_3](Hg_3Cl_8)_2$, long insoluble needles, that decompose in the light, &c.

On the Constitution of Desoxalic Acid, JOSEPH KLEIN (**20,** 146).—In 1861, Loewig, by the reduction of oxalic acid ether with sodium amalgam, obtained a crystalline substance, having the formula $C_{11}H_{18}O_8$, which he regards as triethyl ether of the tribasic desoxalic acid, $C_5H_6O_8$. Brunner, however, regards the same substance as possessing the formula, $C_{12}H_{20}O_9 = C_6H_5(C_2H_5)_3O_9$. The author, on investigation, confirms the results of Loewig in every respect. He has prepared the monacetyl, the diacetyl, the monobenzoyle and the dibenzoyle compounds, in the form of thick, syrupy uncrystalline bodies.

Preparation of Nitro Acids of the Fatty Series, LEWKOWITSCH (**20,** 159).—The author has prepared the corresponding nitro compounds by treating iodo-acetic ether, β-propionic ether and β-propionic acid, with argentic nitrite. The nitropropionic ether obtained is a colorless, mobile liquid, of an etherial odor, that boils at 161–165°. β-nitropropionic acid forms crystals possessing a mother of pearl lustre, that melt at 66–67°. Tin and hydrochloric acid reduce it to β-alanine.

The Teachings of Chemical Valence and their Relation to the Electro-Chemical Theory, ALBRECHT RAU (**20,** 209).—The article does not admit of abstraction.

Contribution to the Knowledge of Sulphoaniline Acid, C. LAAR (**20,** 242).—The author finds that the acid crystallizes in two well defined modifications, the one in rhombic plates with one molecule of H_2O, the other in monosymmetrical plates with two molecules of H_2O. He makes his research, however, more especially on the salts of the acid, and has prepared a number of the same. The soda salt, $Na.C_6H_4.NH_2.SO_3.2H_2O$, crystallizes in leaves; the potash salt, with $1\frac{1}{2}H_2O$, in rhombic prisms; the baryta salt, with $3\frac{1}{2}H_2O$, in rhombic prisms; the copper salt, with $4H_2O$, in blackish-green prisms, that lose their water of crystallization at 100°, and become reddish-brown in color. The aniline salt crystallizes in needles, and on heating to 150° in its dry condition, loses its aniline, and the acid remains behind. The author, however, has more particularly studied the action of phosphorus pentachloride on the potash salt of the sulphoaniline acid. On adding phosphorus pentachloride to potassium sulphoaniline beneath dry benzole, after the evaporation of the ben-

zole, small, spindle-shaped crystals are obtained, that melt at 158°. The body is very unstable. The analysis gives the formula:

$$C_6H_5NSPO_3Cl_3 = C_6H_4\begin{cases}NH.POCl_2\\SO_2Cl\end{cases}$$

In order to prepare the ether corresponding to this chloride, the author heats on the water bath a dry mixture of potassium sulphoaniline with phosphorus pentachloride. The raw product was then poured into absolute alcohol, filtered and mixed with water; by repeating this treatment, long crystalline leaves were obtained, that melted at 102°. The analysis gave the formula:

$$C_{12}H_{20}NSPO_9 = C_6H_4\begin{cases}NH.PO(OC_2H_5)_2\\SO_2.OC_2H_5\end{cases}$$

By pouring the raw product obtained by heating potassium sulphoaniline with phosphorus pentachloride, into absolute methyl alcohol, the corresponding methyl ether is obtained. The latter melts at 114°. On boiling the ethyl compound with water, it is decomposed into sulphoaniline, alcohol and ethyl-phosphoric acid. The last is further decomposed into phosphoric acid and alcohol.

The potash salt of the dibromsulphoaniline, acted on by phosphorus pentachloride, is decomposed by alcohol in the same way, except that only two atoms of chlorine are replaced by the oxy-ethyl. The ether, $C_6H_2Br_2\begin{cases}NH.PO(OC_2H_5)_2\\SO_2Cl\end{cases}$, is mostly decomposed by the simple precipitation with water. The dibromphosphoanilinethersulphochloride melts at 170°, and is easily soluble in acetone, chloroform and benzole.

By the action of phosphorus pentachloride on dimethylsulphoaniline, is obtained the sulpho chloride, out of which is prepared the ethyl ether, $C_6H_4\begin{cases}N(CH_3)_2\\SO_2.OC_2H_5\end{cases}$. The ether is crystalline, and melts at 85°. Dimethylsulphoaniline is decomposed at 230°. Its barium salt is obtained in two modifications.

By oxidizing potassium sulphoaniline with potassium permanganate, potassium salt of azophenyldisulphonic acid was obtained. The salt crystallizes in beautiful, red crystals. They are with difficulty soluble in water, and give with $BaCl_2$ and $AgNO_3$, orange colored crystalline precipitates, which are decolorized on warming with stannous chloride.

On Oxyphenylacetic Acid and its Derivatives, PAUL FRITZSCHE (**20**, 267).—The oxyphenylacetic acid, $CH_2(OC_6H_5)CO_2H$, was prepared by action of sodium phenol on sodium monochloracetate. The free acid crystallizes in long, white needles, having a peculiar

odor and a bitter, sour taste. It is slightly soluble in cold water, easily in hot. The melting point is 96°. A little moisture lowers the melting point perceptibly. It distills without much decomposition at 285°. The distillate remains for a long time liquid and then suddenly solidifies. Ferric chloride produces a yellow precipitate in solutions of the acid. The acid is not poisonous and possesses strong antiseptic qualities. Its salts, especially those of the alkalies, are easily soluble in water; some melt in boiling water, some only above 100°, or not at all.

The methyloxyphenylacetic ether is a thick, oily liquid, of 1.15 sp. gr. It boils at 245°. Its odor is peculiar, but not disagreeable. The ethyl ether has a specific gravity of 1.104, and boils at 251°. When ethyloxyphenylacetic ether is allowed to remain in contact with a strong aqueous solution of ammonia, long needles of oxyphenylacetamide are formed. They are but very slightly soluble in water, and melt at 101.5°. With hydrochloric acid it yields a beautiful crystalline salt. By distilling the amide with phosphoric anhydride, oxyphenylacetonitrile is produced. This last is a clear, oily liquid, boiling at 235–238°, and possessing a specific gravity of 1.09.

When oxyphenylacetonitrile, $C\left(\begin{smallmatrix}H_2\\OC_6H_5\end{smallmatrix}\right)CN$, is warmed with alcoholic ammonia in a stream of sulphuretted hydrogen, oxyphenylacetothioamide, $C\left(\begin{smallmatrix}H_2\\OC_6H_5\end{smallmatrix}\right)CSNH_2$, is produced in the retort. It crystallizes in rhombic prisms that melt at 111°. By boiling with alkalies, it is decomposed into ammonia, oxyphenylacetate and sulphide of the alkali metal.

Finally, when aniline and oxyphenylacetic acid are heated together to 150°, a crystalline mass is obtained, that consists of oxyphenylacetanilide, $C\left(\begin{smallmatrix}H_2\\OC_6H_5\end{smallmatrix}\right)CON\left(\begin{smallmatrix}H\\C_6H_5\end{smallmatrix}\right)$. It crystallizes in needles that melt at 99°.

Orthonitroxyphenylacetic acid was prepared analogously to the oxyphenylacetic acid, by heating orthonitrophenol sodium with sodium monochloracetate. The pure acid crystallizes in small octahedra, that melt undecomposed at 156.5°. It dissolves easily in alcohol, slightly in water. Its color is pale yellow. The salts of orthonitroxyphenylacetic acid are similar to those of oxyphenylacetic acid. The soda salt,

$$C\left(\begin{smallmatrix}H_2\\OC_6H_4NO_2\end{smallmatrix}\right)COONa + H_2O,$$

crystallizes, as do the baryta, copper and other salts.

On reducing this nitro acid with stannous chloride, the anhydride of the amido acid, $C_8H_7NO_2$, is obtained. The anhydride is slightly soluble in water and cold alcohol, but easily in hot alcohol. It crystallizes in small needles, melting at 143–144°, but subliming at a lower temperature. It is soluble in soda or potash, without, however, forming salts. Even boiling potash fails to change it into the amido acid.

The paranitroxyphenylacetic acid, $C_8H_7NO_5$, is prepared exactly in the same way as the ortho compound. It crystallizes in rhombic or monoclinic leaves, and melts at 183°. It is slightly soluble in water, but easily in alcohol. Its taste is bitter and sour. Its aqueous solutions are colored strongly yellow on the addition of alkalies. Its soda and baryta salts are yellow. The copper salt is cerulean blue, but at 150° loses its water of crystallization, and becomes green.

Although it appears that the paranitroxyphenylacetic acid yields, on reduction, a true amido acid, still no satisfactory results could be obtained.

Monobromoxyphenylacetic acid was prepared by the author, by adding bromine to a solution of oxyphenylacetic ether in carbondisulphide, and by saponifying the ether, so obtained, with soda. The monobromoxyphenylacetic acid, $C_8H_7BrO_3$, crystallizes in quadratic prisms, which melt at 153–154°. It is slightly soluble in water, but easily in alcohol. It does not possess so great a tendency to form ethers as the oxyphenylacetic acid. Its soda salt contains $2H_2O$, its baryta salt, $3H_2O$.

Bromoxyphenylacetic ether is made in the preparation of the foregoing. It is insoluble in water, soluble in hot alcohol, and crystallizes in rhombic plates that melt at 59°.

On the Action of the Molten Alkalies on some Aromatic Sulpho Acids, PAUL DEGENER (**20,** 300).—The author continues a former research (Journ. f. prakt. Chem., **17,** 390) on the same subject. The sulpho acid salts were melted, both with potash and soda, as well as with a mixture of the two.

First, in the action of the alkalies on phenolorthosulphonic acid, it was found that the yield of brenzcatechin was best when potash alone was used. The yield also depends upon the temperature as well as the quantity of the potash used. Below 290° no brenzcatechin was obtained, while by heating 24 mols. KHO with 1 mol. $C_6H_4OHSO_3K + 2H_2O$, to 360°, about twenty per cent. of the theoretical amount was obtained. When the heat was continued too long or was too high, the yield was again lower. By heating potash with phenolpara-

sulphonic acid to 360°, nothing was obtained, but at a higher temperature, some phenol and diphenol, but no hydroquinone or resorcine. From benzoledisulphonic acid (1 : 3) potash produces, at a temperature of 270°, resorcine. Soda yields, in all cases, smaller results.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office**, by ARNO BEHR.

June 1, 1880.

228,181.—*Treatment of petroleum lubricating oil and lard oil.* HENRY V. P. DRAPER.

An addition of chloroform to the oil, will keep the oil liquid at a comparatively low temperature.

228,221.—*Paper for bank notes, checks, etc.* JAMES SANGSTER.

Ruling lines across the surface of an ordinary paper with alkali, and then removing or neutralizing the alkali.

228,300.—*Manufacture of artificial indigo-blue.* ADOLF BAEYER.

If a solution of a mixture of orthonitrophenylypropiolic acid, an alkali and glucose, is printed on yarn or cloth, indigo-blue is developed in and upon the fibre by simple application of heat.

228,328.—*Process of making artificial parchment out of toughened paper.* LOUIS H. G. EHRHARDT.

With the paper pulp is mixed silicate of soda, alum and chloride of zinc.

228,362.—*Dry-copying process.* VINCENZ KWAYSSER and RUDOLF HUSAK.

The inventors claim the method of producing on an absorbent surface, possessing the properties of remaining moist and elastic, a transfer impression, reverse from the original writing, and then printing copies from it by pressing dry sheets of paper thereupon.

228,387.—*Process and apparatus for the manufacture of fertilizers.* WM. PLUMER.

Refers to the drying of night soil, and to its transformation into a fertilizer.

228,389.—*Solution for electro-deposition of nickel.* JAMES POWELL.

Claims a mixture of a nickel salt, pyrophosphate of soda or potash, or a mixture of pyrophosphate of soda, phosphate of nickel, bisulphite of soda and citrate of nickel and ammonia.

228,392.—*Process for making illuminating gas.* THOMAS I. F. REGAN.

Claims the process of subjecting naphtha to direct contact with caustic lime within a closed vessel or retort, and drawing off the gas, generated, by an exhauster.

June 8, 1880.

228,463.—*Production of articles by solidifying leather pulp.* JOHN W. HYATT and JOHN H. STEVENS.

After all fat or oil is removed from leather, the latter is dried and ground. The powder is pressed in suitable moulds, heated to 240–250° F., at a pressure of about 5,000 lbs to the square inch.

228,487.—*Refrigerating process and apparatus.* CYPRIEN TESSIÉ DU MOTAY and AUGUSTE T. ROSSI.

228,488.—*Production of cold for manufacturing ice.* CYPRIEN M. TESSIÉ DU MOTAY and AUGUSTE T. ROSSI.

According to claim 5, the inventors propose to use a binary liquid, composed of an absorbent liquid, such as oxalic ether, sulphate of methyl, or other like liquids, having a boiling point above that of water, and sulphurous dioxide.

They also claim the method of safely transporting ethers, by causing them to absorb a quantity of sulphurous dioxide, which will render them uninflammable.

228,519.—*Process and compound for embalming and preserving animal substances.* PETER C. DOREMUS.

The compound to be used for the embalming of dead bodies, consists of a solution of sulphurous acid in water, to which is added saltpetre.

228,615.—*Metallic alloy.* CHARLES I. A. and GEORGE A. DICK.

This alloy is made by adding tin and phosphuret of tin to highly heated wrought iron or iron sponge.

June 15, 1880.

228,804.—*Compound for preserving fruit, etc.* GEO. A. CUTLER.

A mixture of 4 parts of sulphur, 1 of biborate of soda, and 1 of saltpetre, is burned in a closed chamber, in which the fruit is spread on trays.

228,881.—*Preparation of lime-juice.* JOHN and THOMAS D. DOUGLAS.

In order to preserve lime-juice, it is mixed with sugar, water, glycerine, and a sufficient quantity of sulphuric acid.

228,889.—*Process for preparing extract of coffee.* DAVID J. GUE and JOSEPH C. GRANT.

The ground coffee is first extracted with cold, and afterwards with boiling water, and the two extracts are mixed.

228,900.—*Aluminium alloy plating.* JAMES S. HOWARD.

The inventor claims the "solution" of cryolite, chloride of magnesium and chloride of manganese in water, for electroplating.

228,901.—*Fire-brick.* ALFRED E. HUNT.

A composition of 100 parts of pulverized silex and 4 parts of lime.

228,935.—*Deflagrating compound.* JOHN A. ROBINSON and ROBERT H. DIMOCK.

A compound of amorphous phosphorus with plumbic plumbate and chlorate of potassium.

228,955.—*Treatment of sewage.* BRUNO TERNE.

Sewerage water is treated with a solution of superphosphate of lime, and a solution of some material containing tannic or gallic acid.

228,960.—*Roofing and paving material.* CYRUS M. WARREN.

Uses the residuum obtained by the distillation of a mixture of coal-tar, and ordinary petroleum residuum.

228,970.—*Amalgamating metals.* PAUL G. L. G. DESIGNOLLE.

The pulverized ore is thoroughly mixed with a solution of corrosive sublimate, to which is added common salt or hydrochloric acid, and this mixture is subjected to the action of grinding or titrating surfaces of iron, so as to bring each particle of the mixture into intimate contact with iron.

June 22, 1880.

229,038.—*Manufacture of vulcanized india-rubber compounds.* HENRY GERNER.

A new compound called "heveenoid," consisting principally of india-rubber, camphor, sulphur and glycerine.

229,042.—*Compound for preserving food.* GILBERT F. HOLLAND.

2 ounces of alum, 2 ounces of nitrate of potash and 1 pound of gum, are dissolved in 1 gallon of water. The articles of food are dipped into this solution, and the coating dried.

229,045.—*Impervious wrapping-paper.* ROBERT W. JOHNSON.

Claim: The combination of a compound of caoutchouc, and either paraffine or Japan wax, with, and between, two sheets of unsized paper.

229,090.—*Concentrating alkaline solutions.* HUGH BURGESS.

Causing the liquid to trickle down circuitous passages in the presence of heated air, or products of combustion, which are induced to take the same downward course.

229,130.—*Concentrated extract of tobacco.* RICHARD T. HILL.

The tobacco is extracted with water, and a little acid, at a temperature not exceeding 130° F., and the extract afterwards evaporated to the consistency of a syrup.

229,159.—*Compound for fuel and fire-kindlers.* JACOB C. MCCARTY.

A compound for saturating charcoal, coke or coal, to be used as fuel, consisting of a solution of chloride of sodium, sulphate of iron and nitrate of potash.

229,186.—*Filter-paper supporter.* JAMES O. ROBERTSON.

According to the claim it consists of a conical basket, a series of arms extending from its larger end or ring, and a series of projections extending from its lesser ring.

June 29, 1880.

229,248.—*Process of treating pine leaves and other vegetable fibres.* GEORGE T. GREGERSEN.

The claims do not give a sufficiently clear idea of the process.

229,249.—*Manufacture of potassium sulphate from kainite.* CECIL N. HAKE.

If kainite, which is a double salt of potassium chloride and sulphate of magnesium, is dissolved in a hot solution of sulphate of magnesium, schoenite, which is a double salt of potassium and magnesium sulphate, separates on cooling, while chloride of magnesium remains in the mother liquid. The schoenite formed is separated and treated with caustic lime; the product is calcined, and on lixiviation yields a solution of sulphate of potassium.

229,254.—*Mode of converting straw into bleached paper.* JULIUS KAUFFMANN.

First cutting the straw, then boiling it in caustic soda, then separating it from the lye, forming it into cakes, and finally destroying the envelope of, and bleaching, the straw fibre by exposure to chlorine gas.

229,264.—*Recovering soda from spent liquors, after treating vegetable fibre.* CASSIUS C. MARKLE and JOSEPH JORDAN.

The spent soda-lye is evaporated, and caustic lime mixed with it before incineration.

229,274.—*Nickel-depositing solution.* JAS. POWELL.

Benzoic acid is added to the solution of a suitable nickel salt.

229,307.—*Preparing wood for making paper-pulp.* JAMES DAVY, JR.

Removes the bark by a steaming process previous to the reduction of the wood to pulp.

229,308.—*Casting metals.* JAMES DUFF.

The process consists in simultaneously melting and deoxidizing iron or steel, and then casting these metals in an atmosphere free of oxygen.

229,335.—*Carbon for electric lights.* WILLIAM E. SAWYER and ALBON MAN.

Claim: Carbon consolidated and purified by electrically treating it in combination with a carbonaceous substance, for the production of electric burners.

229,338.—*Process and apparatus for producing hydrogen gas.* CYPRIEN MARIE TESSIÉ DU MOTAY.

The process consists, according to the claims, in first highly heating vapor of naphtha and steam; second, bringing the naphtha vapor and steam into contact with a highly heated body of lime; third, passing the gaseous products through a cooler body of lime, whereby carbonic acid is absorbed and separated from the hydrogen; fourth, revivifying the lime when charged with carbonic acid, by burning in its presence a sufficient supply of gas containing hydrogen, and fifth, continuing the operation with the revivified lime.

229,339.—*Process and apparatus for manufacturing hydrogen gas;* and:

229,340.—*Process for the production of hydrogen gas*—by the same inventor—show essentially the same process applied to water-gas and ordinary coal-gas respectively, instead of naphtha.

229,374.—*Apparatus for purifying air.* FRIEDRICK A. BRUNS.

229,473.—*Paint composition.* GENNARO ROSSI.

Consists of refined petroleum, boiled linseed oil, bees wax, sugar of lead, garlic-juice, milk of sulphur, cayenne-pepper and tallow.

Foreign Patents

Condensed from R. BIEDERMANN'S Report to the German Chemical Society, by OTTO H. KRAUSE.

GEO. BORSCHE, Leopoldshall: *Apparatus for the continuous preparation of bromine.* (Germ. P., No. 9553, July 18, 1879.)—The apparatus is a vessel made of sand-stone or other resisting material, containing coke or fragments of earthen ware, &c., through which the solution containing bromine trickles, and meets a current of steam and chlorine gas, which enters near the bottom of the vessel. See also this JOURNAL, **1**, 502.

L. THIERCELIN, Paris: *Method of obtaining iodine, etc., from marine plants.* (Engl. P., No. 2539, June 25, 1879.)—The plants are finely cut up and mashed, and brought to fermentation with the aid of yeast. The alcohol is distilled off, the residue evaporated and calcined at a low temperature. From this iodine, bromine and potassium salts are obtained in known manner.

A. NOBEL, Paris: *Refining cast iron.* (Engl. P., No. 2314, June 11, 1879.) Highly heated hydrogen gas is forced through the molten metal to remove sulphur and phosphorus. Subsequently, superheated steam is passed through, the oxygen of which is supposed to act on the carbon of the cast iron only.

C. DE MONTBLANC and L. GAULARD, Paris: *Removal of metalloids from iron ores and cast iron.* (Engl. P., No. 2383, June 16, 1879.)—These inventors also inject superheated steam into the molten metal. The hydrogen of the decomposed steam is supposed to remove sulphur and phosphorus.

ALFRED NOBEL, Paris: *Explosive compound.* (Engl. P., No. 2399, June 17, 1879.)—The inventor proposes to overcome the difficulty of exploding finely

divided and strongly compressed gunpowder, by placing 3–10 grms of dynamite into the interior of each blasting charge, and by employing a suitable priming composition. For the latter purpose he prefers picrates. 40 parts of bibasic barium picrate, or tribasic lead picrate, are moistened with 3 parts water, and mixed with 60 parts gunpowder, in the form of flour. This mass is made into a cylinder weighing about 6 grms, and set into a cavity left in the charge of compressed gunpowder.

H. F. HOWELL, Sarnia, Ontario, Canada: *Purification of crude petroleum.* (Engl. P., No. 2410, June 18, 1879.)—The petroleum is treated with chlorine. It seems from the somewhat obscure specification, that the inventor not only proposes to remove impurities, such as sulphur and phosphorus, but also to produce substitutions in the hydrocarbons.

J. CAZET, J. LAFAURE, C. JOSSIER and A. MATHEY, Paris: *Method of thickening petroleum and other mineral oils, as well as syrup, by means of lichenin.* (Germ. P., No. 9984, Nov. 7, 1879.)—Japanese moss, or other moss containing lichenin in addition to pectine substances, is extracted with hot water, and the solution intimately mixed with the petroleum. The mass becomes thick or hard, and is rendered easily transportable. By adding alkali and filtering, or by pressing, the petroleum is reobtained in the fluid condition.

JOHN T. KING, Liverpool: *Artificial fuel.* (Engl. P., No. 2521, June 24, 1879.)—Peat, mixed with coal-tar, pitch, asphaltum, lime-stone, salt and borax, in different proportions to suit the purpose for which it is intended.

H. TROTMAN, London: *Gun-cotton.* (Engl. P., No. 2536, June 24, 1879.)—To reduce the degree of explosibility of gun-cotton, it is mixed with "silicate cotton."

E. FARRINGTON, Paris: *Treatment of asphaltum for paving.* (Engl. P., No. 2560, June 26, 1879.)—Instead of softening the asphaltum by means of heat, it is partially dissolved by impregnating the pulverized substance with bisulphide of carbon, naphtha, benzine, etc.

LUDWIG HEYER, Berlin: *Method of recovering caoutchouc from vulcanized rubber waste.* (Germ. P., No. 9910, Sept., 1879.)—The waste is placed in a vessel having three compartments. The steam from the water boiling in the lowest of these, acts upon the rubber contained in the middle one, whilst a higher heat is supplied by a fire in the upper compartment. The sulphur distills off, and the caoutchouc melts and runs into the lowest chamber, the mineral substances being retained upon sieves.

A. ZWILLINGER, Vienna: *Improvements in apparatus for making glue.* (Germ. P., No. 9618, April 19, 1879.)—The apparatus for producing the jelly is composed of two steaming vessels, a steam cylinder and an air compressor. It is so arranged that at no stage of the process can steam and jelly come directly in contact. Compressed air is forced through the bone mass covered with hot water. Yield and quality of the glue are said to be improved thereby.

SIDNEY G. THOMAS: *Phosphates.* (Engl. P., No. 2414, June 18, 1879.)—The slag resulting from Thomas' method of dephosphorizing iron, is finely divided and dissolved in hydrochloric acid. The filtered solution is evaporated, the residue calcined at a temperature sufficient to drive off excess of hydrochloric

acid, without decomposing ferric and manganic chlorides. Water dissolves out calcic, ferric and manganic chlorides, leaving a concentrated basic phosphate.

T. F. WILKINS, London: *Preservation of food.* (Engl. P., No. 2512, June 23, 1879.)—The following chemicals are recommended—chiefly for butter: salicin, methylal, chloral, lactic acid, salicylic acid, metaphosphoric acid, sodium, metaphosphate, borax and sodium formiate.

T. H. GRAY, Clapham: *Manufacture of varnish.* (Engl. P., No. 2518, June 23, 1879.)—Description of an apparatus in which linseed oil can be exposed to the action of a current of heated air.

R. GOTTHEIL, Berlin: *Method of preparing eupittonic acid from wood-tar.* (Germ. P., No. 9328, Oct. 12, 1878.) (See A. W. Hofmann's researches on this coloring matter, Ber. d. d. chem. Gesell., **12**, 1371.)—The part of wood-tar oil which is heavier than water is, after repeated distillations, heated with about 25 per cent. of alkali, the indifferent oils are separated, and the hot alkaline solution mixed with 25 per cent. of sodium chloride. After cooling, the dimethyl ethers of pyrogallic and methylpyrogallic acids separate as a crystalline mass. This is mixed up with about five times its volume of a 20 per cent. solution of sodium hydrate. After heating to boiling, a current of air is passed through the liquid until it becomes perfectly blue. The aqueous solution of potassium eupittonate thereby formed is filtered off hot, and the acid precipitated by addition of hydrochloric acid. The acid is purified by repeatedly recrystallizing its sodium salt.

H. KNOBEL, Leipzig: *Apparatus for continuous extraction.* (Germ. P., No. 9700, Aug. 13, 1879.)—The extracting liquid passes by distillation into the extracting vessels, and from these runs back into the distilling apparatus. The latter is connected with evaporating pans so that the operations of extracting and concentrating go on uninterruptedly.

H. ROHRBECK, Berlin: *Steam dying oven.* (Germ. P., No. 9841, Nov. 4, 1879.)—A drying oven with double walls, between which steam is admitted. Before reaching the drying chamber, the air passes over calcium chloride and through a coil of pipe surrounded by steam and lying on the bottom of the oven. A safety valve and a thermometer are fixed to the apparatus.

W. E. A. HARTMANN, Swansea: *Manufacture of sulphuric acid.* (Engl. P., No. 2839, July 11. 1879.)—The final concentration of the pan acid is carried on in iron instead of platinum vessels. To render this possible, a strong solution of sulphate of iron is added to the acid before it enters the iron pan. Upon further evaporation, the iron salt separates so that only traces of it remain in the acid ultimately drawn off. The iron pan is surmounted by a leaden dome, from which the acid vapors are withdrawn by means of a fan. From the iron pans the concentrated acid flows into a series of leaden vessels, the last one of which contains a leaden cooling worm. In these vessels the sulphate of iron separates almost completely.

FERD. KOPFER, Mannheim: *Method of, and apparatus for, manufacturing chloride of lime.* (Germ. P., No. 9398, Nov. 7, 1879.)—The hydrate of lime is scattered into the chlorine chamber, with the aid of a centrifugal machine fed continuously at the top by a suitably arranged hopper.

FRED. H. MART, Widnes: *Cover for packages containing caustic soda.* (Engl. P., No. 2212, June 4, 1879.)—Relates to the manner of attaching and detaching the inner projections of the cover described in Engl. Pat., 5052; see this JOURNAL, **2**, 70.

H. P. LORENZEN, Friedrichstadt: *Apparatus for, and method of, obtaining ammonia by carbonization of bones.* (Germ. P., No. 9989, Nov. 21, 1879.)—The bones, chiefly for the manufacture of bone-black for sugar refineries, are carbonized in the usual furnaces and pots. The smoke given off at starting is led directly to the chimney, but as soon as gases are evolved, the damper is closed, and the gases passed over lime heated to redness in a reverberatory furnace. Thereby the nitrogenous matters in the vapors are decomposed into ammonia, whilst tar and gases are burned. Thence the gases pass to an iron vessel in which a considerable portion of ammonium carbonate deposits; this vessel is connected with coke towers, through which sulphuric acid trickles and condenses the rest of the ammonia.

HENRY GUTTON, Nancy: *Evaporation of brine.* (Engl. P., No. 2780, July 8, 1879.)—A vertical series of closed vessels containing scrapers, is so arranged that direct fire is applied to the lower one only, the vessels above being heated by the steam given off from the ones below them. Above them all is an open pan.

JOHN B. SPENCE, London: *Compounds of metallic sulphides and sulphur, and separation of metallic sulphides.* (Engl. P., No. 2706, July 3, 1879.)—Iron and copper pyrites in a condition of finest powder, are mixed with from 10 to 40 per cent. of molten sulphur. The cold mass possesses remarkable hardness and metallic lustre, and is of varied applicability.

A. P. G. DAUMESNIL, Paris: *Method of applying a protective coating to metals.* (Germ. P., No. 10059, Oct. 18, 1879.)—The metal is coated with a mixture of platino-chloride of ammonium and borate of lead, and then strongly heated.

RUSSEL AITKIN, London: *Extraction of gases from molten metals.* (Engl. P., No. 2227, June 5, 1879.)—The vessel (mould, crucible, converter) containing the fused metal is connected with an air pump, to remove occluded gases.

JOHN PATTINSON, Newcastle on Tyne: *Manufacture of soluble phosphates.* (Engl. P., No. 2204, June 3, 1879.)—The phosphorus contained in pig iron is to be converted into an alkaline phosphate, by adding an alkaline hydrate, carbonate, sulphate, chloride, fluoride, nitrate or sulphide, to the iron contained in a Bessemer converter having a basic lining.

SAM. HALLSWORTH, Armley: *Purification (?) of illuminating gas.* (Engl. P., No. 2710, July 3, 1879.)—Claims a patent upon mixing pyrites residues with sawdust, moistening the whole with ammonia water, keeping it stored for some time, and then using it for the above purpose.

C. KOMOREK, Oberhausen: *Manufacture of zinc white in a Bessemer converter.* (Germ. P., No. 10079, Jan. 6, 1880.)—Metallic zinc, heated to near its boiling point, is run into a converter kept at a white heat. Zinc white forms upon blowing, and passes through the neck of the converter into a settling chamber. To sustain the high temperature, coal-dust and substances giving off oxygen are to be mixed with the blast air. The bottom of the converter is charged with small coke, when it is desired to make zinc white direct from the ore.

M. E. SAVIGNY and A. C. COLLINEAU, Paris: *Vegetable coloring matter.* (Engl. P., No. 2281, June 9, 1879.)—By extracting alder and birch wood with alkaline lye, and precipitating with an acid, a dark brown substance soluble in water is obtained. The inventors call the coloring matter alnëine.

BINDSCHEDLER and BUSCH, Basel: *Green coloring matter.* (Germ. P., No. 10410, June 10, 1879.)—Tetramethyldiamidotriphenylmethane, obtained from oil of bitter almonds and dimethylaniline, is converted into the sulphonic acid, and the latter oxidized in an acetic acid solution by means of peroxide of lead or manganese.

VICTOR DUCANCEL, Rheims: *Mordant for dyeing on wool.* (Engl. P., No. 2219, June 4, 1879.)—4 parts cupric sulphate, 4 parts ferrous sulphate, 2 parts sulphuric acid at 66°, 3 parts cream of tartar, 1 part alumina, 1 part sodium sulphate, 1 part potassium chromate and 3 parts oxalic acid.

P. MARCELLIN, Dieulefit: *Blue dye for wool.* (Engl. P., No. 2225, June 4, 1879.)—For a deep blue the following materials are used: 10–12 parts extract of logwood, $1\frac{1}{5}$ parts extract of fustic, 12–14 parts sulphate of iron, 10 parts sulphate of soda, 3 parts sulphate of copper, 3 parts bichromate of potash, 24 parts gallnuts and 5 parts aniline blue.

FRANZ DIETRICH, Munich: *Method of working up the mother liquors resulting in the manufacture of tartaric acid.* (Germ. P., No. 10111, Aug. 10, 1879.)—These liquors are said to contain 400–500 grammes tartaric acid per liter. Only 90 per cent. of the free sulphuric acid present is neutralized with lime or chalk, the rest being necessary to retain iron and alumina in solution. To the filtered liquor a solution of neutral potassium tartrate is added, whereby cream of tartar (at 96–99 per cent.) is precipitated; it is filtered off and decomposed with lime in the usual manner.

GUSTAVE VIBRANS, Uefingen: *Clarification of beet juice by means of hydrated silicic acid.* (Germ. P., No. 9664, July 2, 1879.)—The warmed juice is mixed with $\frac{1}{2}$ to 2 liters hydrated silicic acid, at 10° Bé, per 100 liters. Precipitation is then produced by adding lime and heating to boiling.

CHAS. FELHOEN, New York: *Explosive compound.* (Engl. P., No. 2266, June 9, 1879.)—Common gunpowder, but ungrained and unpolished, is mixed with 10 per cent. of nitronaphthalene.

GUSTAVE BISCHOF, London: *Preservation of butter.* (Engl. P., No. 2290, June 10, 1879.)—The butter is covered with a layer of spongy iron and water, so that the air is obliged to pass this layer before coming in contact with the butter.

W. KUBEL, Holzminden: *Disinfecting and fumigating tiles and blocks.* (Germ. P., No. 9520, Sept. 4, 1879.)—Porous tiles of plaster of Paris or earthenware charged with the disinfecting substances.

SCHIPPANG and WEHENKEL, Berlin: *Method of preparing iodized and uniodized cakes of collodion.* (Germ. P., No. 9890, Sept. 12, 1879.)—The collodion cakes are prepared by evaporation and strong pressure, applied simultaneously. A cake of iodized collodion contains layers of common collodion in such proportion, that by dissolving it a uniformly and properly iodized collodion is formed.

THE AMERICAN CHEMICAL SOCIETY.

Cyprien M. Tessié du Motay.

By the death of Mr. Tessié du Motay, this Society has to deplore not only the loss of one of its most distinguished members, but also that of a *savant*, who will leave by his numerous works, discoveries and researches in all branches of technology, a lasting impression on the history of industrial science of our century. He died suddenly, in New York, from apoplexy, at the age of 61 years.

Born in Brittany, France, in 1819, of an old and aristocratic family, Tessié du Motay received in his youth an academical but not technical education. His studies were directed by the famous Abbé Lamennais—a friend of his family, from whom, it must be supposed, he derived his very liberal ideas in politics and philosophy. Gifted with a brilliant and passionate imagination, of a distinguished and at the same time romantic turn of mind, as well as of a superior intelligence, he could not but take an active part in the conflict between the "Romantic" and "Classical" Schools, as the two parties were called, which divided the young generation of *literati* in the first years of the monarchy of Louis Phillippe. Brilliantly endowed as a literary man, his first essays opened to him the doors of the most renowned salons of this period, where French art, literature and science made their abiding place. Even the most exclusive of these opened its doors to one so well fitted to do honor to it, and, in the salon of Mme. Récamier, young Tessié du Motay met with great success in his efforts in the drama, poetry and music. Chateaubriand and Victor Hugo were the familiars of this "Cenacle," and there Tessié du Motay became acquainted with Alfred de Musset, Vigny, Scribe, Theophile Gauthier, Méry, Gérard de Nerval, and all this pleiad of young authors, who have since acquired a prominent place in different branches of literature.

But science had also its fascination upon him: the frequenting of the society of such eminent chemists as Chevreul, Dumas, Berthelot, decided his calling; more especially Chevreul, who was an intimate friend of his father; Chevreul who, at the age of 8 years, held M. du Motay's father in his arms for baptism. Some early discoveries encouraged him to persevere, and finally, by continuous efforts in France and abroad, he conquered for himself a name well known and appreciated in the history of indus-

trial chemistry. Ardent to the task, never sparing the means he had been able to acquire in his professional career as consulting chemist, there has not been a single important subject in technical science developed within the last twenty years, in which Tessié du Motay was not directly or indirectly concerned. Of a generous and open nature, he often gave to manufacturers who consulted him new processes in industry, or happy modifications of old ones, which were applied by them and of which the origin cannot be publicly traced to him.

An ardent and radical republican, brought up in the midst of the liberal agitation of those times, a warm advocate of free speech, free press and free education, he has, in politics, a record that the friends of liberty and liberalism cannot forget. He took, as might be expected, a leading part in all the exciting events of the last years of the Monarchy of July, 1830. He participated, at the side of Ledru-Rollin, in the political movement of 1848, and the subsequent agitation.

Exiled from France, after what is known there as the "Bourgés Trial," in 1849, he went successively to Belgium, England and Germany. In England, he renewed acquaintance with the prominent exiles, Ledru-Rollin, Louis Blanc, Caussidière, Madier de Montjau, all of whom have since become well known.

When abroad, he completed many of his most important discoveries. He returned to France in 1860, and applied himself from that time entirely to industrial chemistry, which secured for him two gold medals and one silver one at the different International Exhibitions in Paris, in 1865 and 1878, and finally, the cross of the Legion d'Honneur. During the siege of Paris he directed the service of the ambulances, and all those who had occasion to know him then, and to see him at work, can testify with what devotion, what cheerful humor and, at the same time, with what patriotism, he took his part in the national defence. He was on the staff of the Governor of Paris, and was present at the most important battles of the siege, that of Champigny, and others.

A literary man, a musician, a philosopher and a *savant*, Tessié du Motay was also one of the most honorable and sympathetic of men. Nobody, better than he, knew how to ally to the genial courtesy and affability of the man of good society, the dignity and the seriousness of a perfect gentleman. The interest and charm of his conversation, the amenity of his intercourse, made him the most fascinating of men, as he was also the truest of friends. Generous, kind hearted, always ready to help misfortune wherever met, during a stay of

hardly eighteen months in this country, he had succeeded in creating around him a circle of appreciative and devoted friends, who held him in the highest regard. Young and old were attracted to him, fascinated, as it were, by the magical charm of his conversation. Even in his later years he did not give up his literary pursuits. He had great fondness for Oriental literature and the mythology and theogony of India. We were fortunate enough to have the privilege to hear him read his translation, or rather adaptation, in French verse (with many original and happy additions inspired by the subject), of some of the songs of Brahma and Vishnu. The enthusiasm of his diction, the genuine animation of his gestures, could well make one believe himself to be transported in reality, into the poetical fictions of Brahmanism and Buddhism. He also left a philosophical drama which he desired should not be published until after his death, which, under the name of the "Expiation of Faust," treats of an old subject in a novel and masterly manner.

HIS SCIENTIFIC WORKS.

It was said of him that he made perhaps more inventions than any other man, for it often happened that when he was consulted about some scientific subject, he would give expression to views so original, and make suggestions so practical, that his consulters often utilized them at once, without his receiving the credit of the suggestion or invention. About 18 months previous to his death, he had come to this country as Consulting Chemist and Engineer of the Municipal Gas Light Company, to superintend the building of retorts and furnaces, and the preparation of machinery for the introduction of the carburetted water gas, practically and on a large scale, for the lighting of this city. Everybody knows what success he has met with. The gas obtained has a much greater illuminating power than the ordinary gas, and can be produced at such reduced rates as to have forced many of the other companies to adopt the process.

Metallurgy.—Metallurgy greatly interested him, and he was intimately connected for the last twenty years with the progress of this science. He patented in England a process for the treatment of arseniferous iron ores, and suggested or made several improvements in the manufacture of ferro-manganese. He was also the first to introduce and manufacture bricks of magnesia for metallurgical purposes. They were made for Mr. de Wendel, in Alsace, for the Siemens-Martins steel furnaces. The magnesia was brought from Eubœa, Greece, in the state of magnesite (magnesium carbonate). The earth was ground, worked in the shape of bricks, which were

compressed by hydraulic pressure of 100 tons. They were then burnt in a kiln at a very intense temperature, so as to prevent the magnesia from changing to carbonate on contact with the air. The best Dinas fire bricks, used at Mr. de Wendel's, lasted generally from 2 to 3 weeks, whereas the magnesia fire bricks of Tessié du Motay lasted 18 months. They were used by Mr. de Wendel in forty reheating furnaces for steel and iron, with great success.

In the fall of 1879, Mr. du Motay was engaged by certain capitalists to make an examination of, and report on, the iron and copper pyrites deposits of Lake Superior and Canada. He was to have undertaken the direction of the reduction of these ores by a new process of his own invention, when death struck him.

Etching on glass.—In collaboration with Maréchal he invented and introduced a very excellent method for etching on glass. The use of hydrofluoric acid is always attended with danger, especially when it is in the gaseous state. But while the solutions of this acid produce on glass brilliant surfaces, it is only by the use of the gas that it is possible to obtain unpolished surfaces, much finer and better adapted for delicate effects in decoration. By his process, excellent results have been obtained, and the dangers of the gas avoided. The hydrofluoric acid is disengaged in the nascent state from a bath composed of fluorhydrate of fluoride of calcium, water, and diluted hydrochloric acid. He recommended also the use of saccharate of lime as a counter-agent against the burns produced by fluorhydric acid.

Photography.—In photography he improved several processes, and, at the same time as Poitevin and Nièpce, made several attempts for the production of colored photographs. In connection with Maréchal he invented a special process for the production of transparent vitrified photographic proofs. A glass plate having been covered with a solution of india-rubber in benzine, and, when dried, with a coating of ioduretted collodion, an image (positive by transparency) is obtained from the negative. After proper treatment by means of cyanide of potassium, platinum and gold baths, to develop and obtain the proper shades of black, the plate is placed in a muffle, and the organic matters burnt. It is then covered with a flux of borax, and vitrified.

Electric light.—Tessié du Motay has been connected with the latest efforts made for the introduction of electric light, on an industrial scale, for illuminating cities. A professional friend of Jablockoff, Moncel and Jamin, and other celebrated electricians, he, with Jablockoff, was the first to suggest the use of carbon pencils coated with kaolin, to prevent their disintegration when burning.

Edison, in his latest electric lamps, realized this idea by using the carbon produced by the calcination of bristol boards; mistaking the true explanation of the case, he attributed to a fourth state of carbon, the peculiar properties of the carbon thus obtained.

Tessié du Motay (in an article which was published in the New York papers) explained that the qualities of durability of these new pencils were due to the presence of kaolin, used for sizing bristol paper, and that he and Jablockoff had many years ago anticipated the idea.

Permanganates.—He gave his attention to the preparation of alkaline permanganates on a large scale, having found an industrial use for them in his new method of preparation of oxygen gas. In the ordinary preparation of the permanganate, peroxide of manganese, chlorate of potash and caustic potash are heated together in an iron retort. After proper manipulations the mass is treated with water, which transforms the manganate into permanganate. Tessié du Motay proposed first to produce the transformation of manganate of potassium into permanganate, by means of sulphate of magnesia. He also obtained the alkaline permanganates by a completely new process, by the action of the oxygen of the air on sesquioxide of manganese in presence of caustic soda or potash. The mixture, introduced into cast iron retorts, is heated to 400° C., and a current of air is passed through the mass.

Preparation of oxygen.—One of his most original, ingenious and successful inventions was that of the preparation of oxygen gas on an industrial scale. His method is based on the following reactions: When the permanganate of sodium or potassium is exposed to a temperature of 450° C., in a current of superheated steam, the salt loses its oxygen, producing caustic alkali and peroxide of manganese. If now this mixture of these two substances, at this same temperature of 450° C., is exposed to the action of a current of air, the primitive salt is regenerated by absorption of oxygen, and can then furnish oxygen anew by the action of superheated steam. In consequence of these successive decompositions and revivifications, a given quantity of permanganate can furnish an indefinite quantity of oxygen. The operation is effected in cast iron retorts. The steam carried away by the oxygen gas is condensed, and the air from which oxygen is to be borrowed for the regeneration of the permanganate, is blown in the retorts after having been deprived of its carbonic acid. By this method one cubic meter of oxygen cost 0.40 francs.

Illuminating gas.—Having thus secured the means of obtaining oxygen cheaply and in great quantities, Tessié du Motay turned his attention to one of his favorite schemes, and one which has brought him a legitimate share of his fame—"a new method of illumination."

In the Drummond light, a mixture of oxygen and hydrogen gas, supplied by two different gasometers, is brought in contact with a cylinder of caustic lime, and lighted. A light, next in intensity to that of the sun or electric arc, is thus produced. Tessié du Motay and Maréchal have rendered this system applicable even to the lighting of cities, by the introduction of their industrial method for the preparation of oxygen gas. Tessié du Motay modified the process in preparing the hydrogen gas, by effecting the decomposition of hydroxide of calcium by carbon in iron retorts. A company, under the name of the New York Oxygen Co., has employed this system of illumination with success for large squares, public places, beacons, signals. It was very much used during the war of secession.

Guided by Caron, Tessié du Motay and Maréchal have since substituted for the calcium pencil a pencil of calcined magnesia, which withstands better the high temperatures which are reached. These pencils having sometimes the inconvenient property of breaking on cooling, they have substituted for them the "zirconia pencils" with much better results.

Tessié du Motay has also introduced a new system of illumination by using water gas (a mixture of hydrogen and carbonic oxide), which is burnt in the presence of a regular current of oxygen, obtained by his process. The flame is directed on cylinders of magnesia and zirconia. This system was tried in Paris, Place de l'Hotel de Ville, in 1868, with success.

In 1870, Tessié du Motay modified his methods in the following manner: He made his oxygen pass into the flame from a solution of naphthalene in petroleum ether. This liquid was called, in France, "carbolene." During the combustion, there are separated from the liquid substances of an intense lighting power. This kind of light is known in France as the "Oxy-carburetted light of Tessié du Motay." The combustion took place in lamps with a wick (Philipp's lamps), into the flame of which the oxygen gas penetrated horizontally.

After these experiments, Tessié du Motay still further modified his system, and gave it a very practical form, by directing a jet of oxygen gas on ordinary illuminating gas from coal, made very rich in carbon by proper carburation, the combustion taking place in a slit burner of steatite. This process was tried in Paris, in 1870, on

the Boulevard de l'Opera, and at the Tuileries, under the auspices of Napoleon III., who was very enthusiastic on the subject. The light, it is said, was intense and really splendid. If it had not been for the complications which the war brought on, this system bade fair, at the time, to be thoroughly tested and employed in Paris. It was on this occasion that he received the cross of the Legion d'Honneur, he having refused it once before, on account of his political record, because it had been officially sent to him. The Emperor gave him an audience, and, having learned his reasons for refusal, took from his coat the cross he was wearing himself and attached it to the bosom of Tessié du Motay, adding that "science and politics had nothing to do together."

Though found objectionable on account of the double system of pipes required, this system of illuminating can be, and, in France, has been, applied in many cases. It has been applied to the lighting of mines, for photography, for sub-marine works, for lighting public places of meeting, theatres, etc. The industrial preparation of oxygen by the du Motay process constitutes certainly a progress very interesting and full of promise for the industry of illuminating gas.

Tessié du Motay still further modified the burner for his gas, by the introduction of his "differential burner." The ordinary illuminating gas, carburetted as before, arrives in two opposite directions by two tubes which are curved horizontally. The oxygen is supplied by a vertical tube reaching slightly below the level of the others, and placed between the two. This burner is formed of several jets of the same kind, placed in a ring. A vertical magnesia or zirconia pencil is slightly engaged at its base in the ring formed by the jets, and becomes incandescent.

Bleaching.—The name of Tessié du Motay is associated with several inventions for the bleaching of textile fabrics and fibers.

In 1874, Tessié du Motay proposed for the scouring of silk (to deprive it of the sericine) the use of a bath of hydrate of baryta (12 to 15 per cent. of the hydrate for 100 of the silk) heated to 80° C. The ordinary decolorizing agents having no action on what is called "gray silk," he proposed to use successively, to bleach these fibers, nascent oxygen gas and sulphur dioxide, sulphydric acid and sulphur dioxide.

The silk is dipped in a solution of permanganate of potassium, and then in a solution of sulphur dioxide, to eliminate the oxides of manganese. After repeated treatments in these solutions, the fibers are introduced into a solution of sulphydric acid, or of alkaline sulphides, washed, and again treated with sulphur dioxide solutions.

For bleaching flax, hemp, cotton, silk and wool, Tessié du Motay has introduced a new method based on the use of the alkaline permanganates. A solution of manganate of sodium is added to a solution of sulphate or chloride of magnesium, or chloride of calcium; by double decomposition, permanganate of sodium, sulphate of sodium, and hydrate of magnesium, or calcium, are produced. The fibers are dipped in the solution. 2 to 6 kgrms of manganate are said to be sufficient for 100 kgrms of cotton, flax or hemp. The fibers are then passed into an alkaline solution, in case of silk or wool in a solution of soap, and afterwards into a solution of sulphur dioxide, to dissolve the oxides of manganese.

The results obtained on a large scale at Comines, France, at the manufactory of Verlay, in 1867, showed that by Tessié du Motay's process, it is possible to bleach completely in a day the fibers of flax and hemp, and that but three days were required for tissues of flax and hemp, and it was claimed that the fibers were no more injured than by the other processes in use, which, moreover, necessitate a much longer time. For 100 m. of linen the cost was stated at six francs. The manganate of sodium could be obtained at one franc per kgrm.

He has also introduced a new method for bleaching wax and feathers, which is at present carried on in France, by Messrs. Viol & Duflot. It is based on the use of oxygenated oil of turpentine.

Industry of sugar (baryta).—In the ordinary process of the treatment of sugar solutions, the sugar is separated from the impurities by the addition of lime and other substances, capable of forming with these impurities insoluble compounds, the sugar remaining in the solution. Dubrunfaut and de Massy have introduced in France a new method of treatment, which is the reverse of the preceding. It consists in separating the sugar from the impurities it contains, by forming with the sugar an insoluble compound, while the impurities remain in the solution. The substance employed is hydrate of baryta, which forms with cane and beet sugar, even at the temperature of ebullition, insoluble saccharate of baryta.

To render this method practicable, hydrate of baryta had to be obtained at a sufficiently low price, and on a large scale. Dubrunfaut and Liplay prepared it by the decomposition of witherite, (barium carbonate) by coal. But this decomposition to be complete, requires the highest temperature, which the kilns used were not able to stand.

Tessié du Motay, in connection with others, has contributed his part to the solution of the problem, and to the introduction of

another and much more economical process. This process has been successfully carried on in France, at Comines (Nord), at Asniéres lès Paris, at Courriére (Pas de Calais), at Menu Tylloy Delaune. It is based on the decomposition of natural barium sulphate (barytes), by coke, and subsequent treatment with zinc oxide.

The mineral is ground, mixed with 20 per cent. of coke or soft-coal, and calcined in a Siemens-Martin furnace. Barium sulphide is thus formed. This sulphide is suspended in water, steam is admitted and the mass is thoroughly agitated. It is then allowed to settle. The supernatant liquid and the concentrated washings of the residue, are received in proper vessels. This liquid is of a complex composition; it contains diluted hydrate of baryta, barium proto and bisulphide, and baryta sulphydrate. The sulphur is eliminated by boiling the liquid, after an addition of zinc oxide (200 kgrms zinc oxide for 35 hectoliters of sulphurous liquid, at 25° B.), the mass being thoroughly agitated all the time. Insoluble zinc sulphide is formed, and baryta hydrate remains in solution. The solutions are concentrated, allowed to crystallize, and the crystals are dried in the "centrifuge." The product is hydrate of baryta with nine equivalents of water. The zinc sulphide is washed, roasted in ovens, and the zinc oxide is thus regenerated for another operation.

Binoxide of barium.—Tessié du Motay, starting from the baryta, has also modified and improved the ordinary process of preparation of bioxide of barium from this base.

Artificial ice.—In 1880, Tessié du Motay and A. J. Rossi patented two new processes for the artificial production of ice and cold, based on the power of absorption, which they find certain ethers and alcoholic radicals to possess, for gaseous sulphur dioxide and ammonia.

In one of them, a mechanical power is used to produce the volatilisation of both constituents of the binary liquid, the vapors of which are compressed under very small pressures in a condenser, where the ether liquifies easily, absorbing the vapors of sulphur dioxide, reconstituting the original liquid, and thus avoiding the high pressures necessary to liquify the sulphur dioxide by mechanical compression.

In the other, advantage is taken of the higher point of ebullition or less volatility of the absorbing ether. No mechanical power is required. The sulphur dioxide is disengaged by the action of heat (a water bath), from the absorbent contained in a boiler, and condensed to the liquid state, by proper cooling and the pressure the gas exerts on its own molecules.

The fire being removed from the boiler, and the latter cooled in its turn, the liquid dioxide evaporates under the partial vacuum thus produced, generating an intense cold, its vapors being absorbed as fast as they are formed by the absorbent in the boiler, working much in the same manner as the Carré ammonia solution machines, but with much less pressure, and with a water bath instead of a furnace.

In 1879, Tessié du Motay, in collaboration with L. F. Beckwith, took out in this country several patents of a mechanical character, for small rotary motors, for mechanical devices, for the application of the cold produced by refrigerating machines to the ventilation and cooling of mines, for improvements in steam condensers used on board of steamers, by using a very volatile liquid, such as sulphur dioxide, for condensing steam, instead of water, the volatile liquid being thereby volatilized under high pressures, the mechanical action of which could be utilized on a piston so as to restitute part of the mechanical power otherwise lost in the condensing water. He also took a patent with L. F. Beckwith, for the joint use in the same ice machine, of sulphur dioxide and choride of methyl, with the idea of using the former as an extinguisher of the latter.

New York, July, 1880. AUGUSTE J. ROSSI.

XXXIII.—Examination of the Raw Materials Used for the Arita Porcelain.

By Nawokichi Matsui, Ph.D.

It has been asserted by several writers, that the raw materials used in the manufacture of porcelain, in Japan and China, are somewhat different from those chosen for the same purpose in Europe; but, as this assertion seems to owe its origin to the examination of a few isolated specimens, and, also, to the casual observations made by the travelers in those countries, it is exceedingly interesting for us to make a more extended and complete examination of them, and to compare them with those used in Europe, after long years of experience. The samples that form the subject of my present investigation have come from Koransha, a large porcelain manufacturing company of Arita, in the province of Hizen. As this locality has been the great centre of this industry in Japan for about three hundred years, the examination of the raw materials used there will also give a tolerably good idea of those generally used in Japan, although in other places a slight variation in their choice may naturally be expected. The native minerals are all said to be found in the neighborhood of the village Arita, and mostly in one hill, called Idsunuyama. They are all white, varying considerably in hardness, and apparently showing different stages of the decomposition of the felspathic rocks. They are as follows:

1. Tsuji-ishi,
2. Shiro-tsuchi,
3. Midsuana-ishi,
4. Kudakè-ishi,

} For the body of the ware.

5. Composition for the body of the superior kind of the ware.
6. Composition for the body of the inferior kind of the ware.

7. Genyemon-ishi,
8. Rikita-ishi,
9. Haruji-ishi,
10. Tai-ishi,

} For the glaze.

11. Seiji-ishi, for the glaze of the Seiji, or the Seladon ware.
12. Yusu-bai, or the ash obtained from the bark of the *Ficus pyrifolia*, used in compounding the glaze.
13. The glaze composition for the ordinary ware.
14. The Seiji glaze composition.
15. Nakadaru-tsuchi, used in a thin layer between the body and the glaze.
16. Gosu, or the pigment for the cobalt blue.

In order to obtain the average composition as nearly as possible, it was deemed advisable to take about one-half pound of each sample, and to crush it by the Blake's crusher when necessary, and then to grind by means of the steel plane-roller used in assaying; the ground mineral was then sifted, taking care to use all the material, and then the powder was well mixed. A small quantity of each was specially ground to an impalpable powder, in an agate mortar, and was used for the analysis. It is not necessary to give the detailed description of the method of the analysis pursued in the following examinations, but it may be stated, that the general scheme for the analysis of iron slag was followed, except the precipitation of the $Al_2O_3 + Fe_2O_3$, for which $(H_4N)HO$ was used, instead of $Na_2C_2O_4$, and the filtrate was evaporated to dryness and ignited, to drive off the H_4N salts, in order to precipitate MnO_2 by Br. The Al_2O_3 and Fe_2O_3 were weighed together, and were afterward fused with $NaHSO_4$ and brought into solution, from which the iron was titrated with $K_2Mn_2O_8$. S was determined in the filtrate from the MgO precipitate. It was found necessary to deduct a small quantity of S from each result, as the flux always contained some sulphur. For the alkali determination, Wurtz's modification of Dr. J. Lawrence Smith's method (described in the *American Chemist*, **7**, 6) was followed. After weighing KCl and NaCl together in a platinum dish, KCl was precipitated with $PtCl_4$, and was weighed as $Pt + 2KCl$. This last process was found, after a trial, to give as accurate a result as weighing Pt alone, and saves us the trouble of washing away KCl, and also from the danger of losing some Pt in that operation. The densities were all determined in powder at 15° C., and those given in the following pages are each the mean of two or more determinations.

1. Tsuji-ishi. This is used for making the body of the best kind of the Arita ware, after it is crushed and washed, mostly mixed with other minerals. It is a grayish-white mineral, showing distinctly soft and hard layers. In powder it turns slightly pink on ignition. The fresh surface does not soil the finger when touched. It has an odor somewhat resembling that of chalk, and feels gritty between the teeth. Small crystals of pyrite are found disseminated through the mass. It adheres very slightly to the tongue, but is quite tough. When heated with dilute HCl, it gives off H_2S. The fracture is sometimes uneven and sometimes conchoidal. Hardness = 4; den-

sity = 2.679. This is the most refractory mineral in the whole series. The following is the composition.

H_2O	3.31
SiO_2	76.74
Al_2O_3	13.75
FeS_2	.81
FeO	.55
MnO	.06
CaO	none
MgO	.11
K_2O	3.87
Na_2O	.69
	99.89

Calculating the proportions of SiO_2 and Al_2O_3 necessary to saturate the alkalies above found, in order to form felspar [$(KNa)_2O.Al_2O_3.6SiO_2$], and then estimating again the necessary proportions of H_2O and SiO_2, combined with the remaining Al_2O_3 in kaolin, whose formula is here assumed to be $Al_2O_3.2SiO_2.H_2O$, we have obtained the following remarkable result:

Felspar	$(KNa)_2O$	4.56	28.73
	Al_2O_3	5.37	
	SiO_2	18.80	
Kaolin	Al_2O_3	8.38	21.09
	SiO_2	9.78	
	H_2O	2.93	
Free SiO_2			48.16
FeS_2, FeO, MnO MgO and H_2O			1.91
			99.89

This cannot be considered as a mere coincidence, as a similar result can be obtained from each of the following analyses. It is more remarkable if we reflect for an instant that the compositions of these minerals (kaolin and felspar) are somewhat variable, even when the purest specimens are selected. The excess of .38 per cent. of H_2O may be due to the hygroscopic moisture, or it may be in combination with SiO_2.

2. Shiro-tsuchi. This is also used for compounding the body, and is whiter and less refractory than No. 1. It becomes slightly pink on ignition. It contains hard, irregular grains scattered through the mass. It is softer than No. 1, and the fresh surface soils the finger. It has

chalky odor and crushes grittily between the teeth. It gives off H_2S when heated with diluted HCl. Pyrite is found in irregular masses. Fracture, uneven. Hardness = 3. Density = 2.657. The analysis gave:

H_2O	3.58
SiO_2	74.28
Al_2O_3	15.14
FeS_2	1.69
FeO	.50
MnO	.07
CaO	.23
MgO	.03
K_2O	4.02
Na_2O	.71
	100.25

By calculating as before, we obtain:

Felspar	$(KNa)_2O$	4.73	29.79
	Al_2O_3	5.57	
	SiO_2	19.49	
Kaolin	Al_2O_3	9.57	24.17
	SiO_2	11.27	
	H_2O	3.33	
Free SiO_2			43.52
FeS_2, FeO, MnO, CaO, MgO, H_2O			2.77
			100.25

3. Midsuana-ishi is used, like the two preceding minerals, for compounding the body, and is added to make it more fusible. It is almost white, having less grayish tinge than Nos. 1 and 2, but turns decidedly pink on ignition. The fresh surface soils the finger when touched, and crushes grittily between the teeth. It has an earthy odor and adheres to the tongue. By scratching with a knife hard and soft layers can easily be detected. Small crystals of FeS_2 are found on the surface, and the specimen is, in some portions, colored yellowish-red with the hydrated oxide of iron. It gives off H_2S when heated with diluted HCl. Fracture, uneven. Hardness = 4. Density = 2.541.

The analysis gave:

H_2O	3.05
SiO_2	75.76
Al_2O_3	13.56
FeS_2	.36
FeO	.62
MnO	.18
CaO	.29
MgO	.12
K_2O	5.03
Na_2O	1.50
	100.47

From which, calculating as before, we get:

Felspar	K_2O	5.03	42.45
	Na_2O	1.50	
	Al_2O_3	7.98	
	SiO_2	27.94	
Kaolin	Al_2O_3	5.58	14.04
	SiO_2	6.51	
	H_2O	1.95	
Free SiO_2			41.31
FeO, FeS_2, etc			2.68
			100.48

On comparing this result with the two preceding, it is evident that the greater fusibility of this mineral is due to the presence of the larger percentage of felspar and the less of kaolin, while the refractory character of No. 1 is greatly enhanced by the large amounts of the free SiO_2.

4. Kudakè-ishi, or the powder stone, probably so named from the readiness with which it is ground. Although it is used for the same purpose as the three foregoing, it comes from Shirakawayama, and differs from them in this respect as well as in some physical characters. It is a white mineral with a light grayish tinge, and becomes slightly yellow on ignition. It easily breaks to powder, which is unctuous to the touch. It is not at all gritty between the teeth, and the fresh surface soils the finger. It has an earthy odor, and adheres to the tongue strongly. The fracture is sometimes even and sometimes uneven. Pyrite is not visible, though it gives off H_2S. It is quite fusible. Hardness = 1.5. Density = 2.602.

The analysis gave the following composition :

H_2O	3.60
SiO_2	73.36
Al_2O_3	14.03
FeS_2	.06
Fe_2O_3	1.38
MnO	.07
CaO	.24
MgO	.43
K_2O	4.99
Na_2O	1.62
	99.78

From which we obtain :

Felspar	K_2O	4.99	43.16
	Na_2O	1.66	
	Al_2O_3	8.08	
	SiO_2	28.47	
Kaolin	Al_2O_3	5.95	14.98
	SiO_2	6.95	
	H_2O	2.08	
Free SiO_2		37.92	
FeS_2, Fe_2O_3, etc.			3.72
			99.78

5. and 6. These are both the prepared materials, ready to be made into any desired shape. They are both white, 6 being slightly yellower than 5. They are slightly gritty between the teeth. Boiled with diluted HCl, 5 gives off H_2S, but 6 gives none.

The analysis gave :

	5.	6.
H_2O	4.70	4.64
SiO_2	72.96	72.19
Al_2O_3	16.84	16.53
Fe_2O_3	.46	.76
SO_3	.52	.67
MnO	trace	trace
CaO	.27	.31
K_2O	3.87	4.03
Na_2O	.29	.44
MgO	.07	.07
	99.98	99.64

From which, by calculation as before, we derive the following:

	5.	6.
Felspar	25.35	27.23
Kaolin	30.56	28.43
Free SiO_2	42.31	41.27
Fe_2O_3, SO_3, etc.	1.77	2.71
	99.99	99.64

It is here to be remarked that, though the percentage compositions of these prepared materials do not materially differ from those of the previous minerals, the effects of crushing and washing, which these minerals have undergone in reaching this state, are more clearly seen from the figures above given. It is hardly necessary to say that the proportion of kaolin has been considerably increased, and that of felspar decreased, as would naturally be expected; while the amount of SiO_2 remains about the same as before in both specimens. However, it must not be passed unnoticed that the foreign impurities, like MnO_2 and FeS_2, have been largely removed, and the remaining iron and sulphur are in the oxidized state.

The difference observed between 5 and 6 is apparently very slight; yet the inferiority of 6 to 5 is no doubt due to the greater fusibility, and also to the little more iron contained in 6, which would probably make it less white.

7. Genyemon-ishi. This is used for making the glaze, together with the three others which follow it, and is the most refractory of all the glaze stones. It is grayish-white and remains so after ignition. It is apparently homogeneous in texture, except that the black grains of pyrite are found disseminated through it. It is not so tough as 8 and 9. It attracts the tongue and feels gritty between the teeth. Its odor is earthy, and the fresh surface does not soil the finger. It gives off H_2S when heated with diluted HCl. Its fracture is even. Density = 2.574. Hardness = 3.5. Its composition is as follows:

H_2O	2.40
SiO_2	77.74
Al_2O_3	13.35
FeS_2	.05
FeO	.71
MnO	.01
CaO	.21
MgO	.05
K_2O	5.05
Na_2O	1.29
	100.30

Computing as before, we have:

Felspar	40.71
Kaolin	14.35
Free SiO_2	43.81
FeO, CaO, etc.	1.43
	100.30

8. Rikita-ishi is used for compounding the glaze as the preceding It has about the same color as 7, but turns very slightly pink on ignition, owing to the presence of pyrite. It is apparently homogeneous, except that FeS_2 is found in thin layers on the surface. It slightly adheres to the tongue, and feels gritty between the teeth. The fresh surface does not soil the finger, and its fracture is sometimes even and sometimes uneven. Boiled with diluted HCl, it gives off H_2S. It has an earthy odor. Hardness = 4. Density = 2.608. The following is the composition:

H_2O	2.42
SiO_2	77.38
Al_2O_3	13.30
FeS_2	.24
FeO	.73
MnO	trace
CaO	.39
MgO	.08
K_2O	4.62
Na_2O	1.15
	100.31

Calculating as before, we obtain:

Felspar	37.06
Kaolin	15.98
Free SiO_2	45.63
FeO, CaO, etc.	1.64
	100.31

9. Harujisugu-ishi. This is also used for the glaze, and is added to the preceding to make the mixture more fusible. It is grayish-white, but turns slightly pink on ignition, like 8. When it is scratched with a knife, the distinct layers of hard and soft matter can be easily made out The fresh surface does not soil the finger, but

slightly adheres to the tongue. It has an earthy smell, and feels gritty between the teeth. The mineral is covered with the black spots of pyrite and also a soft yellow mineral, containing iron and sulphuric acid, which is probably melanterite, formed by the oxidation of pyrite. The fracture is sometimes uneven and sometimes conchoidal. It gives off H_2S when heated with diluted HCl. The harder portion of this mineral is the hardest in the whole series, its hardness varying between 4.5 and 5.5. Density = 2.447. The analysis gave:

H_2O	2.56
SiO_2	75.10
Al_2O_3	13.64
FeS_2	.96
FeO	.59
MnO	trace
CaO	.49
MgO	.15
K_2O	4.53
Na_2O	2.39
	100.41

Computing as before, we have :

Felspar	43.42
Kaolin	12.03
Free SiO_2	41.88
FeS_2, etc.	3.08
	100.41

10. Tai-ishi. This is also used for the glaze, although it differs in many respects from the preceding three minerals. It is the whitest mineral in the whole series, and shows no change of color on ignition, as the amount of iron is very small. It is homogeneous in texture, and breaks to powder readily. It feels slightly gritty between the teeth, and smells earthy. No pyrite is visible, but gives off a trace of H_2S when treated with diluted HCl. It is very porous and adheres strongly to the tongue. The fresh surface smears the fingers. Its fracture is uneven. Hardness = 3. The powdered mineral is

unctuous to the touch and is quite fusible. Density = 2.618. The analysis gave:

H_2O	2.72
SiO_2	77.74
Al_2O_3	13.64
FeO	.37
S	trace
MnO	.08
CaO	.23
K_2O	.73
Na_2O	4.36
MgO	trace
	99.87

From which we derive:

Felspar	41.25
Kaolin	14.18
Free SiO_2	43.01
FeO, etc.	1.43
	99.87

11. Seiji-ishi. This is used for the light green glaze of the Seiji or Seladon ware. It is laminated, and the softer laminæ are highly colored with the hydrated oxide of iron. In powder it somewhat resembles litharge in color, and its color becomes darker on ignition. Its fresh surface does not soil the finger, but sticks slightly to the tongue. It is tougher than the preceding glaze minerals, and is gritty between the teeth. It is quite fusible, and is probably less decomposed than any mineral in the whole series. Fracture, uneven. When treated with HCl, it gives off H_2S. Hardness = 3.5. Density = 2.596. The analysis gave the following result:

H_2O	1.84
SiO_2	74.45
Al_2O_3	13.45
FeS_2	.19
Fe_2O_3	1.60
MnO	.05
CaO	.63
MgO	.03
K_2O	4.54
Na_2O	2.75
	99.83

From which we obtain:

Felspar	49.63
Kaolin	10.18
Free SiO_2	37.10
Fe_2O_3, etc.	2.92
	99.83

12. Yusu-bai, or the lixiviated ash obtained from the bark of the *Fiscus pyrifolia*. This is used in compounding the glaze to make the washed glaze stones much more fusible. It looks like common wood-ash and contains some unburnt charcoal. Water dissolves out $CaSO_4$ and a small quantity of K_2CO_3 and Na_2CO_3. This was ignited in a platinum dish in order to burn up all the charcoal, and the resulting substance was analyzed. The following composition was obtained:

SiO_2	32.83
Al_2O_3	3.83
Fe_2O_3	.99
SO_3	1.27
MnO	trace
CaO	29.57
MgO	trace
K_2O	.35
Na_2O	.07
CO_2 (calculated)	23.44
H_2O and loss	7.65
	100.00

13. The glaze composition. It is grayish compared with the body compositions, owing, no doubt, to the presence of the Yusu-bai. It effervesces when treated with HCl. The analysis gave:

H_2O	3.66
SiO_2	56.23
Al_2O_3	13.48
Fe_2O_3	.59
SO_3	.93
MnO	trace
CaO	5.14
MgO	.05
K_2O	2.43
Na_2O	2.69
CO_2 (combined with CaO, and calculated)	4.10
	99.20

From the comparison of the above analysis with the compositions of the preceding glaze minerals and the ash, it may safely be inferred that the great increase in fusibility, resulting from the addition of the ash to the washed glaze minerals, is due to the presence of 5.14 per cent. of CaO which has come almost entirely from it. Omitting from the foregoing analysis the H_2O, SO_3 and CO_2, which will no doubt be expelled in the oven, and computing the remainder to 100, we get the following for the approximate composition of the glaze mixture after fusion:

SiO_2	73.09
Al_2O_3	14.88
Fe_2O_3	.65
CaO	5.67
MgO	.06
K_2O	2.68
Na_2O	2.97
	100.00

It will be seen that this does not differ materially from the composition of ordinary glass, though in the latter Al_2O_3 is much lower, and the alkalies are generally higher in the percentage.

In order to find out the approximate composition of the washed glaze mineral before the addition of the ash, 17.5 per cent. of each constituent of the ash has been subtracted from the corresponding one of the glaze composition, to eliminate nearly all the CaO which has come from it; and for the remainder, computed to 100, we have:

H_2O	2.96
SiO_2	73.31
Al_2O_3	15.53
Fe_2O_3	.52
SO_3	1.19
MnO	trace
CaO	.29
MgO	.06
K_2O	2.88
Na_2O	2.26
	100.00

From which we obtain, as before:

Felspar	44.66
Kaolin	17.55
Free SiO_2	35.21
Fe_2O_3, etc.	2.58
	100.00

Here it must be remembered that this does not show the composition of any one of the washed glaze minerals, but rather that of the mixture of two or more; yet I think it is sufficient to show the change which the native minerals undergo during the process of crushing and washing, and it is safe to conclude that kaolin and felspar are increased, while the percentage of SiO_2 is decreased.

14. The composition for the Seiji glaze. It is grayish-yellow in color, and feels slightly gritty between the teeth. It effervesces with acid. The analysis gave:

H_2O	4.12
SiO_2	65.69
Fe_2O_3	1.46
SO_3	1.27
MnO	trace
CaO	5.39
MgO	trace
K_2O	3.90
Na_2O	2.37
CO_2 (calculated)	4.28
	100.01

Omitting the H_2O, CO_2 and SO_3, and computing the remainder to 100, we obtain the following for the composition of the Seiji glaze after fusion:

SiO_2	71.71
Al_2O_3	13.89
Fe_2O_3	1.67
CaO	5.88
K_2O	4.26
Na_2O	2.59
	100.00

It will be seen from the above analysis that the light green color of the Seiji glaze is due to the Fe_2O_3, whose quantity in this glaze exceeds that in the ordinary white glaze, by about one per cent.

By subtracting the ash, amounting to 17.5 per cent. of the glaze composition, and then computing the result to 100, we obtain for the composition of the mineral after washing:

H_2O	3.44
SiO_2	72.48
Al_2O_3	14.48
Fe_2O_3	1.60
CaO	.60
K_2O	4.58
Na_2O	2.82
	100.00

From which we derive:

Felspar	50.98
Kaolin	12.08
Free SiO_2	32.98
FeO_2, etc	3.96
	100.00

The concentration of kaolin and felspar is here less than in the case of the ordinary glaze, but the free SiO_2 has been removed to nearly the same extent as before.

15. Nakadaru-tsuchi. This mineral differs considerably from the preceding series in being more thoroughly decomposed. Its use is also peculiar, and it is applied in a thin layer between the body and the glaze, in order to give the smooth surface necessary to fine porcelain, and also to make it possible to obtain the beautiful blue of the Gosu. It has light cream color, and shows no apparent change in color on ignition. It crushes to soft powder between the fingers, and the fresh surface soils the finger. Its powder is unctuous to the touch. It has chalky odor and is not gritty between the teeth. It falls to powder in water and is almost as plastic as true clays. It adheres to the tongue strongly, and has a slight astringent taste like alum, owing to the presence of sulphate of iron, which can be extracted with water. It gives off no H_2S with acid. Fracture, uneven. Density = 2.716, being the highest in the series. Hardness = 1.5.

The analysis gave:

H_2O	8.79
SiO_2	47.38
Al_2O_3	33.24
FeO	1.68
SO_3	1.95
MnO	trace
CaO	.59
MgO	.04
K_2O	5.31
Na_2O	1.38
	100.36

From the large percentages of Al_2O_3 and H_2O in the above analysis, it is clear that this mineral is very rich in kaolin. After deducting 60 per cent. of kaolin, containing 8.35 per cent. H_2O, and also all FeO and SO_3, from the above analysis, that which remains has about the same composition as oligoclase, in which K_2O largely takes the place of Na_2O. Hence it may be inferred that this mineral is a mixture of the following:

Felspar	35.66
Kaolin	60.00
FeO, etc.	4.70
	100.36

16. Gosu, or the substance used for the beautiful cobalt blue that is applied generally under the glaze. This has no connection with the foregoing minerals. It is imported into Japan from China, and the mode of manufacturing it is not known. It comes to market in dark olive green lumps, and is very hard to grind. It is almost insoluble in acid, and had to be fused with soda to get it in solution.

The analysis gave the following composition:

H_2O (moisture)	1.68
SiO_2	4.97
$Fe_2O_3 + Al_2O_3$	28.70
Mn_3O_4	45.24
CoO	19.05
	99.64

It is astonishing what a large percentage of Mn_3O_4 there is in the substance, and that it does not seriously interfere with the blue color imparted by 19.05 per cent. of CoO.

Though no analysis of the Arita porcelain itself has been made in the present investigation, the approximate composition may be obtained by subtracting from the analysis of the body compositions given under 5 and 6, SO_3 and H_2O, which are no doubt driven off during the process of baking, and then computing the results to 100. They are as follows.

	5	6
SiO_2	77.00	76.53
Al_2O_3	17.77	17.52
Fe_2O_3	.48	.86
CaO	.29	.33
MgO	.07	.07
K_2O	4.08	4.27
Na_2O	.31	.47
	100.00	100.00

ANALYSES OF EUROPEAN AND ORIENTAL PORCELAIN.

Analysts.	Laurent.	Laurent.	Müller of Prague.	Vielguth.	Salvétat.	Salvétat.	H. Wurtz.	H. Wurtz.
Kind of Ware.	Sèvres.	Vienna of 1806.	Berlin.	Nymphenberger.	Chinese, 1st Qual.	Chinese, 3d Qual.	Japanese Egg-shell Ware.	Japanese Thick-bodied.
SiO_2	58.0	61.5	71.34	72.80	69.00	73.3	78.763	74.545
Al_2O_3	34.5	31.6	23.76	18.40	23.60	19.3	17.847	19.315
Fe_2O_3	....	.8	1.74	2.50	1.20	2.0	.638	.916
CaO	4.5	1.8	.57	3.30	.30	.6	.213	.106
MgO	....	1.4	.19	.30	.02	trace	.029	.176
Na_2O	....	....	.58	1.84	2.90	2.9	1.975	2.832
K_2O	3.0	2.2	2.00	.65	3.30	2.5	.203	.566
Totals	100.0	99.3	100.18	99.79	100.32	100.6	99.668	99.568

The preceding analyses show that the peculiarity of the Japanese porcelain consists in the relatively large amount of SiO_2, together with the small percentage of Al_2O_3, while CaO is present only in a very small quantity. It is to be remarked that this last peculiarity is shared by the Chinese porcelains also, at least, of the superior quality. Thus far I have occupied myself with the description and the analysis of each individual sample, without much reference to their relation to each other; and I now pass on to the discussion of their relative fusibility. This was determined by heating the same quantity (.5 grm) of each sample in powder, over a blast lamp, for a given time (7 min.), in a platinum crucible, conducting the experiment in the same way as much as possible. The resulting masses were examined carefully as to the relative coherence. The most refractory minerals were found after the above operation to be in about the same condition as before, while the most fusible one turned partly to white enamel. The numbers given in the succeeding table indicate nothing more than the order in which they stand with regard to refractory character.

Minerals.	Densities.	Kaolin.	Felspar.	Free SiO_2	CaO.	Hardness.	Fusibility.
15. Nakadaru-tsuchi ...	2.716	60.00	35.66	....	.59	1.5	9
5. Body composition..	2.664	30.56	25.35	42.31	.27	...	1
1. Tsuji-ishi	2.679	21.09	28.73	48.16	....	4.0	2
6. Body composition..	2.663	28.43	27.23	41.27	.31	...	3
2. Shiro-tsuchi.....	2.657	24.17	29.79	43.52	.23	3.0	4
8. Rikita-ishi	2.608	15.98	37.06	45.63	.39	4.0	7
7. Genyemon-ishi	2.574	14.35	40.70	43.81	.21	3.5	5
10. Tai-ishi	2.618	14.18	41.28	43.30	.23	3.0	11
3. Midsuana-ishi	2.541	14.04	42.45	41.31	.29	4.0	6
4. Kudakè-ishi.....	2.602	14.98	43.16	37.92	.24	1.5	10
9. Haruji-ishi.....	2.447	12.03	43.42	41.88	.49	4.5-5.5	8
11. Seiji-ishi.....	2.596	10.18	49.63	37.10	.63	3.5	12

On carefully examining the above table, it will be observed that the higher the percentage of kaolin and the lower that of felspar, the greater the density; and that the larger the amount of felspar, the

greater is the fusibility. There are some remarkable exceptions to these general rules, which are only apparent, and in reality conform to them. Thus, in the case of Nakadaru-tsuchi (15), notwithstanding the large percentage of kaolin, and consequently the high density, it is very fusible, owing to the large amount of the alkalies contained in the felspar. In Tai-ishi (10), the comparatively high density and the great fusibility are both due to the presence of the large amount of the soda-felspar, which is more fusible and has generally higher density than the potash-felspar; while in Kudakè-ishi, the high density is caused by kaolin. For the high density of the Seiji-ishi, no reason is apparent but the probable difference in the manner of the composition, and hence in the molecular structure, as this, together with Nakadaru-tsuchi (15) and Kudakè-ishi (4), do not come from the Idsumigama quarries like the rest. It is also to be remarked that though the absolute quantity of CaO in these minerals is small, it seems to have some influence on the fusibility, for the relatively high percentage of CaO is here associated with the more fusible of the minerals, while the most refractory raw mineral does not contain it at all.

Most careful search for crystalline structures in the thin sections of these minerals, by the aid of a microscope with ordinary light, has been in vain; but polarized light brought to view a very few small fragments, which are probably broken crystals of felspar, in only three specimens, viz.: Tsuji-ishi (1), Genyemon-ishi (7) and Rikita-ishi (8). As these fragments are found not in the least decomposed, they rather seem to be the accidental than the normal constituents. It is surprising to find how thorough is the loss of crystalline structures in these minerals, while so much of the alkalies, and presumably the felspar, is retained.

XXXIV.—Contributions from the Chemical Laboratory of the University of Michigan.

By Albert B. Prescott.

IV. Proportion of nitrogen compounds in the grain and flour of different varieties of wheat.

The first six of the analyses numbered below are taken from the record of some analytical work which I did at the request of the Michigan State Millers' Association, in the last ten days of July, 1877. The samples of these six varieties were all furnished me, at that time, by the Secretary of the Association, Mr. W. Hibbard, of Grand Rapids, Michigan. The report of these analyses was received at the meeting of the Michigan Millers' Association, held in Detroit, August 1, 1877, and was published, with the proceedings, in the Detroit daily papers of that date. In that report, the percentages of albuminoids were computed by multiplying the nitrogen percentage by 6.45. Below, to make the results uniform with later analyses, I use 6.25 as the ratio of albuminoids to nitrogen. Thus, the nitrogen of No. 1 was found to be 2.067 per cent., and the albuminoids of No. 1 were reported to the Millers' Association as 13.33 per cent., while given below as 12.919 per cent.

The analyses given below for Nos. 7, 8 and 9, were made by Mr. Sylvester J. Heimbach, at Ann Arbor, in the spring of 1879, and have not been published before. The samples of grain and flour were furnished to Mr. Heimbach* as follows:

No. 7, "White Amber," by Wm. Frame, Hamansville, Mich.; No. 8, Red Wheat, "Fulce," by Lantz & Brown, Constantine, Mich.; No. 9, "Clawson," by D. Frazier, Constantine, Mich. Great care was taken to obtain pure and genuine samples of these varieties of the grain; and the flour of each variety was taken after the mill had been running for some time on the same variety.

The work upon No. 10, grain and flour, was done by Mr. F. D. Merritt, at the University, in June, 1880. The grain and both flours of No. 10 were furnished to Mr. Merritt, with due precautions, by a miller whose address I am not able to find. The "patent flour" was understood to have been ground down, from the middlings of No. 10, by a process now well known to millers, for the "patent flour" of the market. Its high percentage of nitrogen corresponds to the exceeding tenacity of its sponge and porosity of bread and crusts baked from it. The middlings are made to give up a part of that rich

*The present address of Mr. Heimbach is Oak Bluffs, Mass.

layer of albuminoid cells which lies so close to the woody husk, that it goes most easily to the bran.

The Michigan Millers' Association, in August, 1877, published a resolution unfavorable to the quality of Clawson wheat flour, and expressing a decided opinion that the extensive raising of this variety of wheat in the State, would injure the reputation of Michigan flour wherever it would go. This opinion was based only in part upon the results of the chemical analyses, and in part (as appeared from the report of the meeting) upon other evidences then adduced. The farmers of the State, as far as represented in the papers, generally resisted the conclusions of the millers, and pretty actively attacked the chemical analyses and all other statements adduced by anybody to the disadvantage of Clawson wheat flour. The violence of the discussion in the public prints drew my attention to the matter, and I have since been observant of all evidences as to the import of nitrogen percentage in measuring the bread-making strength of flour. So far as I can ascertain, the proportion of nitrogenous compounds is an unfailing, practical measure of the capacity of flour to make light bread, and to make large and heavy loaves from a given weight of flour. Porous bread holds a heavy percentage of moisture, without appearing to be moist, and it is the gluten that sustains porosity. The quantity of gluten is represented—practically, though not absolutely—by the quantity of nitrogen. And, it may be suggested, that the market value of flour depends upon its bread-raising strength, and the whiteness of its bread, rather than upon its nutrient capacity.

PERCENTAGES IN ENTIRE GRAIN.

	Of grain dried at 100° C.		Moisture lost in drying at 100° C.
	NITROGEN.	ALBUMINOIDS.	
No. 1. "Gold Medal" Wheat, Michigan, 1877.....	2.067	12.919	13.55
No. 2. "Crescent Mills" Wheat, Michigan, 1877....	1.713	10.706	10.76
No. 3. "Diehl" Wheat, Michigan, 1877.....	1.789	11.181	12.35
No. 4. "Tapahanock" Wheat, Michigan, 1877.....	2.516	15.725	11.70
No. 5. "Clawson" Wheat, Michigan, 1877.....	1.680	10.500	11.35
No. 6. "Treadwell" Wheat, Michigan, 1877.....	2.400	15.000	10.74
Mean of the six varieties....	2.027	12.672	11.74

PERCENTAGES IN ENTIRE GRAIN AND IN FLOUR (AIR-DRY).

	In Entire Grain.		In Flour.	
	NITROGEN.	ALBUMINOIDS.	NITROGEN.	ALBUMINOIDS.
No. 7. "White Amber" Wheat, St. Joseph Co., Mich., 1878, on sandy soil (Heimbach).....	2.013	12.581	1.963	12.269
No. 8. "Fulce" Wheat (red), St. Joseph Co., Mich., 1878, on sandy soil (Heimbach).....	1.993	12.456	1.900	11.875
No. 9. "Clawson" Wheat, St. Joseph Co., Mich., 1878; very rich soil, half prairie and half "opening" (Heimbach).	1.794	11.212	1.650	10.312
No. 10. Red Winter Wheat, 1879 (Merritt)	2.096	13.104	1.963	12.271
"Patent Flour" from No. 10 (Merritt).....	....	....	2.040	12.750
Mean of Nos. 7, 8, 9 and 10 (not including "Patent Flour" of 10)	1.974	12.338	1.869	11.682

All the nitrogen determinations were made by the soda-lime process. Those for Nos. 7 to 10 were made in triplicate operations, with the following results in *percentages of nitrogen.*

	1st.	2nd.	3rd.	Mean.
No. 7. Grain.	2.02	1.98	2.04	2.013
Flour	1.99	1.96	1.94	1.963
No. 8. Grain.	2.01	1.90	2.08	1.996
Flour.	1.87	1.92	1.91	1.900
No. 9. Grain.	1.80	1.76	1.82*	1.794
Flour.	1.62	1.70	1.63	1.650
No. 10. Grain.	2.08	2.10	2.11	2.096
Flour.	1.96	1.95	1.98	1.963
"Patent Flour."	2.04	2.03	2.05	2.040

V. ANALYSES OF VINEGAR.

The following examinations were made by Mr. John P. Kelly, in May and June, 1879. The *percentage of acetic acid* was found by

* For No. 9 grain, a fourth trial gave 1.79, and a fifth gave 1.80. The mean above is that of the five operations.

simple acidimetry, except when sulphuric acid was present. In this case, the total acid was first taken ; then the vinegar was evaporated to dryness on the water bath, and several times the evaporation repeated with previous additions of water, when the fixed acid in the residue was determined, and this subtracted from the total acid first found. Examination for *aldehyde* was made in a distillate, obtained at about 20° C., by addition of potassium hydrate solution, leaving several hours for the appearance of the brown "aldehyde resin." The idoform test was applied for *alcohol.* The estimation by Fehling's solution was made directly for *sugar*, and therefore the results are a little too high, as other reducing agents must slightly increase the reduction of the copper.

Examination for *free sulphuric acid* was made by three qualitative tests:

1. The *ash* was moistened and tested with litmus, when an alkaline reaction should be obtained if no free mineral acid were present.

2. The vinegar was evaporated, the residue extracted with alcohol, the alcohol removed from the extract by evaporation, and test applied by barium salt and free acid, when a precipitate can be determined gravimetrically (J. T. King, Chem. News, **25**, 227).

3. The addition of ammonium oxalate solution to two portions of the vinegar, with addition of ammonium hydrate to one portion. A decidedly greater turbidity in the last named portion indicates mineral acid (Thresh, Pharm. Journ. Trans. (3), **6**, 1, July 3, 1875; Journ. Chem. Soc., **29**, 107).

No mineral acids were found, except a trace of free sulphuric acid in No. 5.

The ash was tested for *poisonous metals*, and none were found except lead in traces in No 2.

	Name of vinegar.	Per cent. of acetic acid.	Presence of aldehyde.	Presence of alcohol.	Per cent. of sugar.	Sugar in grains per gal.
No. 1.	White Wine.	3.24	A little.	None.	0.09	55
" 2.	Cider.	4.20	Abundant.	"	0.10	63
" 3.	"	3.26			0.08	52
" 4.	White Wine.	3.79	Traces.	Traces.	0.06	39
" 5.	" "	5.60	A little.	"	0.12	74
" 6.	" "	3.96	"	None.	0.06	39
" 7.	Cider.	3.96	"	"	0.11	66
" 8.	"	3.60	Abundance.	Traces.	0.11	67
" 9.	"	6.60	"	"	0.14	85
" 10.	"	4.40	Traces.	None.	0.06	37
" 11.	White Wine.	4.80	"	"	0.10	59
Mean.....		4.29				

The names of the manufacturers are given in Mr. Kelly's report, preserved at the University.

VI. TEST LIMITS IN THE EXAMINATION OF SUGAR FOR INJURIOUS METALS.

Mr. A. L. Walker made a series of trials to ascertain the least proportion of tin salts that could be detected in white sugars. The sugar was dissolved in distilled water, to make a thin syrup; this was acidulated with hydrochloric acid, and then washed hydrosulphuric acid gas was passed through, for half an hour. No coloration or precipitate appearing, solutions of tin salts of known strength were added, and the treatment repeated. The precipitate was filtered out and washed, and the tin estimated as dioxide. First was tried the addition of one part of stannous chloride to 14,000 parts of sugar; 0.004 grm of $SnCl_2 2H_2O$ to 56 grms sugar; the proportion of one grain of tin salt to two pounds sugar. In the first operation, $\frac{14}{28}$ of the tin was recovered; in a second, $\frac{2}{28}$ of the tin was recovered. Two experiments were made with stannic chloride, with about the same results. Then, for qualitative purposes, one part of tin salt was added to 56,000 parts of sugar (one grain to eight pounds), and a distinct light-brown precipitate obtained. With one part tin salt to 112,000 parts of sugar (one grain to sixteen pounds), a distinct coloration, but no precipitate, was obtained. Parallel trials with stannous and stannic salts gave the same result. And this was accepted as the qualitative limit, to establish negative results, as to presence of tin in white sugars.

Some time ago I reported similar determinations of limits of delicacy of tests of sugar for lead by hydrogen sulphide, and for arsenic by sodium amalgam, to obtain arsenious hydride in reaction with silver nitrate* (Am. Journ. Pharm., **49**, 487, Oct., 1877; analyses by Messrs. Johnson and Parkill). Placing all the results together, we have the following comparison of tests of sugar, *by methods without destruction of the organic matter.*

QUALITATIVE LIMITS FOR NEGATIVE RESULTS.

Arsenic,	one	grain	of	the	element	in	476	pounds	sugar.
Lead,	"	"	"	"	metal	"	10	"	"
Tin,	"	"	"	"	salt	"	16	"	"

*The thin syrup, made slightly alkaline with fixed alkali hydrate, is placed in a half-liter flask, with addition of sodium amalgam, to cause a slow evolution of hydrogen, and left several hours, while the mouth of the flask is covered by a disk of filter paper wet with silver nitrate solution, and held down by a watch glass.

A positive result, at these limits, would, of course, be ambiguous; and a larger proportion of either metal would be required to enable the operator to identify it positively by these methods.

Methods by destruction of the organic matter—besides requiring great labor, and involving much danger of contamination from the chemicals and the exposure—can hardly reach the limit of delicacy attained with these simple methods.

Twenty-six samples of sugar, taken from the market, were subjected to examination, by the method above described, and no indication of the presence of tin (or lead) was obtained.

VII. ESTIMATION OF NICOTIA IN TOBACCO.

Some work was done by Mr. E. T. Pease, in the estimation of alkaloid in leaf and manufactured tobacco, by the volumetric method with potassium mercuric iodide, as directed in detail by Dragendorff (Werthbestimmung einiger starkwirkenden Droguen, 1874, 52).

The tobacco was first dried, the portion weighed, then macerated for at least twenty-four hours with water acidulated with sulphuric acid, and the expressed liquid concentrated and filtered. The solution from 2 to 3 grms of tobacco, was brought to 50 c.c., and of this 10 c.c. were taken for titration. The end of the reaction was found by filtering a few drops through a very small filter, trying the filtrate on a watch glass with a drop of the volumetric reagent, and rinsing the filter into the whole solution. The potassium mercuric iodide was twentieth normal, or old decinormal, Mayer's standard ($HgCl_2 + 6KI$).

The precipitate first obtained appears milky when formed, but soon turns black and waxy, and settles to the bottom in a coherent mass. Several of the operations were duplicated, with but very slight differences in results. The end of the precipitation is sharply defined.

No. 1. Cigars ..... 2.00 per cent. nicotia.
No. 2. Kentucky leaf tobacco ..... 4.05 " " "
No. 3. Sweet peach chewing, manufactured, with much steaming, from same grade as No. 2. 3.24 " " "
No. 4. Filler from real Havana tobacco cigar. 4.21 " " "
No. 5. "Havana-seed" leaf tobacco (grown in this country from imported seed)..... 3.94 " " "
No. 6. Gem cigarette tobacco, Richmond, Va. 3.93 " " "

A short clay pipe, some time in use and partly colored, though not darker than pipes seen on the street daily, was pulverized, macer-

ated in acidulated water, and the solution treated as from tobacco. The result of titration, if due to nicotia, indicated 0.4779 grm of that alkaloid. The pipe weighed 23.619 grms; therefore 2.02 per cent. of alkaloid were indicated.

Mr. Pease also made an experiment in determination of tobacco smoke. The presence of nicotia in the smoke has been made the subject of discrepant reports. I report the following result, also the one with the old pipe, above stated, with some reservation. At present I am not assured but that some of the empyreumatic products of nicotia (or of tobacco) may react with Mayer's solution. Until research or experiment settles the question, I could not interpret the results as positive evidences of unchanged nicotia. A quantity of the dried Havana-seed leaf tobacco (No. 5), weighing 3.6685 grms, was burned in a brier-wood pipe (one long in use). The pipe bowl was tightly connected to glass tubing reaching to the bottom of a four ounce flask, containing acidulated water, and this flask was suitably connected with another holding acidulated water. All the smoke was drawn through the flasks. The filtered solutions were concentrated, and titrated. A total of 0.081 grm of nicotia was indicated, this being 2.48 per cent. of the dried tobacco burned.

VIII. ESTIMATIONS OF ARSENIC IN WALL PAPER, GREEN TARLETAN, AND GREEN CAMBRIC.

Mr. Arthur S. Parker found the following proportions of arsenic in wall papers of green and drab colors:

In One Square Yard.		In Equivalent of Arsenic Anhydride.
No. 1	contained	0.520
" 2	"	1.296
" 3	"	0.216
" 4	"	0.900
" 5	"	0.792
" 6	"	2.260
" 7	"	4.840
" 8	"	0.324
" 9	"	4.312

Of nine samples of tarletan, only two were found to contain arsenic, and these in proportions too small for determination.

Two samples of green cambric were found to contain arsenic, the one giving 4.000 grms, and the other 3.879 grms, per square yard.

The arsenic was dissolved from the fabrics by treatment with hydrochloric acid. From the filtered solution, the copper was precipitated by excess of potassium hydrate. The filtered liquid,

acidulated, was now treated with hydrogen sulphide, and the precipitate oxidized with nitric acid, and heated on the sand bath, to vaporize sulphuric acid and dispel organic matter, the residue being weighed as arsenic anhydride (Vaughan's method, *Am. Chemist*, 7, 348, March, 1877).

IX. EXAMINATION OF PICKLES FOR COPPER.

Mr. Edwin Hawley subjected fifteen samples of grocers' pickles to an analysis for copper and other poisonous metals. They were obtained in Michigan, except two samples which were furnished by Chicago dealers. Only one sample was found to contain copper, and this was in an enormous amount. From 5.909 grms of pickle (drained, but not dried), the weight of cuprous sulphide was 0.0755 grm. This gives over four per cent. (4.58 per cent.) of crystallized copper sulphate in the pickle. The pickles of this sample left a decided copper deposit upon a bright knife, upon a few minutes contact. In the examination, the pickle was dried, and ignited in a porcelain crucible, with additions of sulphuric acid. The residue was treated with dilute nitric acid and water, and the resulting solution charged with hydrosulphuric acid gas. Negative results showed absence of lead, etc., as well as copper.

XXXV.—Note on the Determination of Alcohol with Cobalt Sulphocyanide.

By T. T. Morrell.

In the *American Chemist*, 6, 370, I published a process for the determination of alcohol, based upon the use of cobalt sulphocyanide. A. Vogel has lately experimented in the same direction, and observes that approximate results may be reached. As I think the principle capable of giving very exact results, I trust that I may be permitted a few words of explanation.

The method as published, directed to place a measured quantity of the dark blue alcoholic solution of sulphocyanide, of standard strength, in the testing tube, and pour the sample to be examined upon it, until just the faintest blue color remained, matching a strip of pale blue glass. This method had the advantage that the temperature was not much altered by the treatment, but had the disadvantage that the red tint of the aqueous sulphocyanide, which decidedly tones the last traces of the blue, was differently diluted in treating samples of different richness. This I overcame, at first, by

using several pale colored solutions by which to measure the final tint, suitably graded in shade, and each representing a range of about 10 per cent. of alcohol. This I could easily do, as the color of the alcoholic sulphocyanide is absolutely unalterable, if the tube be hermetically sealed and kept in the dark.

However, I have lately worked in a different way where great accuracy was required. I put the measured standard blue into a tube $1\frac{1}{2}$ inches in diameter and 10 inches long (with a bottle neck and ground stopper for shaking), and mark the tube about five inches from the bottom, to indicate the amount of liquid to be used in the test. A quantity of the alcoholic liquid to be tested, is now poured upon it, to observe how rapidly the color disappears. If it disappears at once, 95 per cent. of alcohol is run in from a burette until it is restored. This alternate treatment with the sample liquid and the 95 per cent. alcohol, is repeated until the mark on the tube is almost reached. The proper temperature is now obtained, and the few drops required to reach the mark, and correct the depth of tint, are added. If the solution tested is, on the other hand, too strong, distilled water is used instead of the 95 per cent. alcohol. In this way, the final tint is the same in every experiment.

It is always easy to hit the true percentage (ether, amylic alcohol, etc., being absent, to 0.25 per cent., and even much closer results may be got in samples of low percentages, by using a larger amount of the standard blue.

Many substances in solution in the sample, have no effect upon the color, and by this method distillation is often saved. I pointed out in the original paper, how liquors colored with caramel could be treated directly.

I may add that I have successfully titrated minute quantities of silver nitrate in absolute alcohol, with this standard blue, the blue color persisting, of course, when the silver was all thrown down.

The reaction may be also used to determine traces of cobalt in the double cobalt and potash nitrite, since a little free hydrochloric acid does no harm.

Abstracts from American and Foreign Journals.

Journal of the Chemical Society (London)

Abstractor, ARTHUR H. ELLIOTT, F.C.S.

A Chemical Study of Vegetable Albinism, Part II, Respiration and Transpiration of Albino Foliage, A. H. CHURCH (1880, 1).—In this paper the author has sought to determine "The exact relation of equal areas of white and green foliage to carbon dioxide, oxygen and moisture." White foliage has not the power of decomposing carbon dioxide, either in strong daylight or actual sunshine; but adds largely to the normal amount of that gas in the air, thus behaving like flower petals. The plants experimented upon were *Cyperus alternifolius, Acer negundo, Ilex aquifolium, Hedera helix* and *Alocasia macrorhiza.* The first of these gave indecisive, and the last yielded the best, results. When the otherwise white leaves contained green patches, these were "stopped out" by painting with collodion. The leaf-stalks placed in tubes containing recently boiled, distilled water, cooled out of contact with the air, were arranged under a bell-jar, so that the air from the leaves could be made to pass through a Pettenkofer's absorption tube containing baryta water.

The loss of water suffered by albino leaves, as compared with green ones, was also studied, using white and green holly leaves. When these were placed in water, the green leaves gained 1.55 per cent., and the white ones 0.29 per cent.; while without water, the white leaves lost 6.54, and the green ones, 10.26 per cent. of their original weight, in 3¼ hours under the same circumstances.

On Alpha-methylhydroxysuccinic Acid, the Product of the Action of Anhydrous Hydrocyanic Acid upon Ethylacetoacetate, GEORGE H. MORRIS (1880, 6).—The author of this paper has gone over the work of Demarçay, who describes this body as oxypyrotartaric acid. The acid and its salts were prepared, the acid reduced with fuming hydriodic acid, and the products of its dry distillation examined.

The acid was prepared by heating a mixture of two parts of pure ethylacetoacetate and one part of anhydrous hydrocyanic acid, in sealed tubes for three days, at 100°; heating the resulting product on a water bath till hydrocyanic acid was expelled, and then boiling with dilute hydrochloric acid till the decomposition was complete. The acid was finally purified by treatment with ether, precipitation of the

coloring matters with basic lead acetate, evaporation of the etherial solution, and drying over sulphuric acid in a vacuum. So obtained, the acid was a crystalline mass, very deliquescent, easily soluble in alcohol and ether, and crystallizes from these solvents in star-like groups of needles. It melts at 108°, and decomposes at a higher temperature. The barium, calcium, potassium, silver, lead and copper salts of this acid, are described by the author. The free acid gives no precipitate with neutral or acid lead acetate, but is completely precipitated by the basic acetate. A solution of a neutral salt of this acid gives a precipitate with basic lead acetate, and also with silver nitrate; but with neutral lead acetate, or barium hydrate, it gives no precipitate.

The conclusion drawn from the action of fuming hydryodic acid upon this acid is, that pyrotartaric acid is first formed, which under the influence of hydryodic acid, splits up into either butyric or isobutyric acid, and carbon dioxide.

By dry distillation it was found that the acid decomposed at about 140°, carbon dioxide, with a little carbon monoxide, and an acid, watery liquid, being the products. When the acid had been heated to 200°, and the evolution of gas had ceased, the temperature was raised to 210–215°, and a yellow oil distilled over. When the oil ceased to come over, nothing but a black, coaly residue remained. The watery distillate contained acetic acid and methylic alcohol. The yellow oil proved to be citraconic anhydride, giving silver and lead salts identical with those formed from known citraconic acid.

Contributions to the History of Putrefaction, Part I, C. T. KINGZETT (1880, 15).—The details of a number of experiments upon putrefaction are given, and also the results of the action of potassium permanganate upon organic bodies, both fresh and in various stages of decomposition. The experiments prove that putrefaction can begin and proceed in the absence of oxygen, as such. In some experiments the putrescible solutions used slightly more oxygen, from potassium permanganate, after a time than at the start, and some of them used less. Finally, in the putrefactive process there comes a time when the activity of the agencies at work diminishes, and finally ceases.

These experiments have a direct bearing on the oxygen process of water analysis, and show that the amount of oxygen that a water takes up from potassium permanganate, even if it contains organic matter, does not give any idea of the degree of decomposition such organic matter has undergone.

Notes on Manganese Dioxide, C. R. ALDER WRIGHT and A. E. MENKE (1880, 22).—The experiments described are a continuation of the "Second Report on Some Points in Chemical Dynamics," published in the *Journal* (1878, 504). Manganese dioxide was prepared according to the following methods:

1. By the action of nitric acid upon potassium permanganate. 2. From manganese superchloride by precipitating with water. 3. By the action of sulphuric acid on potassium permanganate. 4. By the action of sulphur dioxide on potassium permanganate. 5. By the action of alcohol or glycerine on potassium permanganate. 6. By the action of potassium permanganate on manganese sulphate. 7. Manganese superoxide prepared by the action of air and caustic potash upon manganese chloride. 8. Manganese dioxide precipitated by bromine in presence of potassium acetate. 9. Manganese dioxide from manganese nitrate by heat.

From an examination of the preceding products, the authors arrive at the following conclusions: The manganese dioxide prepared by precipitation is a hydrate (MnO_2H_2O) which loses its water at ordinary temperatures. Neither at ordinary temperatures, at 100°, nor at 210°, does this hydrate become anhydrous. At ordinary temperatures, and at 100°, there is no material loss of oxygen; but at 210°, oxygen is slowly given off. The substance made by heating manganese nitrate does not lose oxygen thus.

Hydrated manganese dioxide, prepared in presence of potassium salts, invariably carries down more or less potash. K_2O varies from 2.50 to 14.85 per cent. of the dry manganese dioxide. And when the precipitation takes place under such conditions, that not much potash (or other metallic oxide) can be carried down, a deficiency of oxygen is noticeable in the precipitate MnO being carried down.

The precipitate formed by reducing potassium permanganate with sulphur dioxide, alcohol or glycerine, contains much less available oxygen than corresponds to the manganese present.

The substance formed by heating manganese nitrate to 160° is free from combined potassium, even if much potassium nitrate is present.

Hydrated manganese dioxide, heated for a long time in hydrogen, loses all or nearly all the potash, leaving green MnO behind.

Manganese monoxide, prepared by heating in hydrogen, but not long enough to expel all the potash, frequently oxidizes spontaneously in ordinary moist air; while that free from potash does not so oxidize.

Manganese chloride is sensibly volatile in a stream of hydrochloric acid gas, at a red heat.

The Comparative Value of Different Methods of Fractional Distillation, FRED. D. BROWN (1880, 49).—The author divides the methods of fractional distillation into two classes; those in which the vapors are passed through layers of the condensed liquid are called *washing methods*, and those in which the vapors are cooled by coils kept at a given temperature, are called *cooling methods.*

Distillations of mixtures of carbon disulphide and benzine were conducted in an apparatus called a dephlegmator, by which the vapors were washed; and also in a flask containing a tube to hold a thermometer, and having a lateral branch bent upward to hold another thermometer, and this branch again having a lateral tube to conduct the vapors to the condenser.

After reducing the results obtained from these two apparatuses to a common form, and also those obtained by distillation from a retort, and from a flask with T-piece without the upward bend, the author represents the results in a diagram of curves. From these curves it appears that the simple T-piece used to insert the thermometer, had considerable influence on the distillation; that both the dephlegmator and cooling tube gave better results than the retort and the flask with simple T-piece; and finally, that the distillation with cooling tube bent upward was rather better than with the dephlegmator.

The author also experimented upon the effect of rapidity of distillation on the results, using a special form of dephlegmator. By distilling a mixture of carbon disulphide and benzine, it was found that the slower the distillation, the more carbon disulphide was in the distillate.

Experiments made with a coil apparatus capable of being maintained at a given temperature, showed "that when the still head is maintained at a temperature equal to the boiling point of the most volatile compound in a mixture, that compound alone, or nearly alone, passes over into the condenser." By using this apparatus, the author has separated benzine from commercial benzine, and always in a nearly pure state.

On the Influence Exerted upon the Course of Certain Chemical Changes by Variations in the Amount of Water of Dilution, M. M. PATTISON MUIR and CHARLES SLATER (1880, 60).—The authors have determined by a number of experiments, the influence of variations in the quantity of water in the system, $CaCl_2 + Na_2CO_3 + xH_2O$; and also in the reaction, $BaCl_2 + K_2C_2O_4 = BaC_2O_4 + 2KCl$. In the first case they find, that the amount of chemical change in a given

time decreases regularly as the amount of dilution increases; and suppose that the chances of collision between the molecules of sodium carbonate and calcium chloride are decreased, the greater the number of inactive water molecules interposed.

In the second case, the same conclusions were drawn from the same circumstances; but when the temperature of the vessel in which the change proceeded, was decreased, it was found that the amount of chemical change in the same time, is retarded to a proportionately greater extent by a large than a small quantity of water of dilution. And when the change is allowed to proceed for a long time, there is the same irregularity in the action of the diluting water. The same results are obtained when the temperature is allowed to rise to 16° or 18°.

The authors ascribe this increased retarding action of large masses of water, to the formation of hydrates of barium chloride, and consider the cryohydrate as the most important. At moderate temperatures, this cryohydrate has least chance to form, and there results a regular action in the water of dilution. But at low temperatures, cryohydrate tends to form, and being produced in the presence of a large mass of one of the products of its own dissociation, it is stable. The greater the mass of water, the greater the stability of the cryohydrate, other conditions being constant.

The authors think that the irregularity in the amount of chemical change in the barium system with various masses of water, is due to a state of strain between its parts; and the principal forces are, the force tending to produce cryohydrate molecules, the force tending to split up these molecules, and the force tending to separate the the chemically active molecules of the system.

The paper is illustrated with a number of diagrams of curves, showing the amount of chemical change under various circumstances.

On the Influence of Temperature upon the Decomposition of Barium Chloride by Potassium Oxalate in Aqueous Solution, M. M. PATTISON MUIR (1880, 78).—The solutions used, and the methods employed, were the same as in the preceding paper. The influence of temperature begins to be felt when 300 c.c. of water of dilution are added; the increase in the amount of chemical change is considerably greater for the rise of temperature from 3° to 20°, than for that from 20° to 80°. When 600 to 700 c.c. of water are added, the increase in the amount of chemical change is very small for the first 20°, but after that the increase is rapid.

In concentrated solutions, temperature exerts very little influence on the amount of chemical change under consideration; in more

dilute solutions, an increase of 20° makes a marked increase in the amount of change; but after this the influence of temperature is regular. With yet more dilute solutions, increase of temperature causes, at first, a slight increase in the amount of chemical action. As the temperature rises, the amount of action rapidly increases, until a point is reached where increase of temperature but slightly affects the amount of chemical change. With very dilute solutions, the influence of temperature becomes very nearly regular.

On Alpha- and Beta-Phenanthrenecarboxylic Acids, with Remarks on the Constitution of Phenanthrene, FRANCIS R. JAPP (1880, 83).—In the preparation of calcium phenanthrene-sulphonate, the author noticed that there was a relatively small yield of crystals, and much dark colored mother liquor. From the crystals, alpha-phenanthrenecarboxylic acid was obtained, by converting them into a sodium salt, distilling the latter with potassium ferrocyanide, and saponifying the nitrile obtained. The acid thus obtained has been described by the author in conjunction with Dr. Schultz (Ber., **10**, 1661); and the author gives the melting point of the purified acid as 266°, instead of 260°.

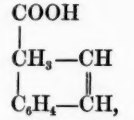
From the dark colored mother liquor, mentioned above, the author has prepared beta-phenanthrenecarboxylic acid, which is isomeric with the alpha compound. The mother liquor was treated with sodium carbonate until alkaline, then filtered from calcium carbonate, and evaporated to dryness. The dried sodium salt was mixed with potassium ferrocyanide, and distilled. The nitrile obtained was yellow, transparent, viscid, and became like butter after some days. It was saponified with alcoholic potash, and boiled until ammonia ceased to be evolved; and the new acid separated by acidifying with hydrochloric acid, as a dirty white precipitate. 2 kilos of commercial phenanthrene gave 80 grms of the crude acid. By making the sodium salt of this acid, and repeatedly crystallizing, the white acid was obtained by treatment with hydrochloric acid.

Beta-phenanthrenecarboxylic acid is soluble in alcohol, ether, and glacial acetic acid, almost insoluble in water. It melts at 250–252°. The author's formula is $C_{15}H_{10}O_2$, for the acid; $C_{14}H_9CO_2Na + 5H_2O$, for the sodium salt; and $(C_{14}H_9CO_2)_2Ba + 6H_2O$, for the barium salt.

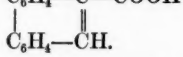
The beta-phenanthrenecarboxylic acid obtained as above, gave phenanthrene on heating with soda-lime; and the quinone obtained from the phenanthrene by oxidation, dissolved without residue in acid so-

dium sulphite. By oxidizing the new acid with chromic acid in acetic acid solution, phenanthrenequinone was obtained.

From the above and some previous results of the author, he considers the following points of theory: Since alpha-phenanthrenecarboxylic acid yields phenanthrenequinonecarboxylic acid on oxidation, the carboxyl group remaining intact, the formula of alpha-phenanthrenecarboxylic acid is



and, since beta-phenanthrenecarboxylic acid gives phenanthrenequinone on oxidation, eliminating the carboxyl group, the latter must be attached to one of the carbon atoms united with quinonic oxygen in the quinone. This would make the formula of beta-phenanthrenecarboxylic acid,



After reviewing much past work done on this subject, the author considers that phenanthrene consists of three benzine neucleii, one of which shares four adjacent carbon atoms with the two others—one ortho pair with each.

On some Derivatives of Phenylacetic Acid, P. PHILLIPS BEDSON (1880, 90).—NITRO-DERIVATIVES. Phenylacetic acid, when nitrated, yields two isomeric derivatives, the para and the ortho.

1. *Paranitrophenylacetic acid* is soluble in hot water, from which it crystallizes in long needles; it is sparingly soluble in cold water, and easily in alcohol and ether. The formula found is $C_8H_7NO_2O_2$. When oxidized with potassium bichromate and sulphuric acid, it yields paranitrobenzoic acid.

Methylparanitrophenylacetate, $C_6H_4.NO_2.CH_2CO_2CH_3$, crystallizes from alcohol, and melts at 54–55°. Ethylparanitrophenylacetate also crystallizes from alcohol, and melts at 62–64°.

Paramidophenylacetic acid, $C_6H_4.NH_2.CH_2CO_2H$, is prepared by the reduction of the paranitro acid by tin and hydrochloric acid. It melts at 199–200°, with decomposition. Analysis gave $C_8H_9NO_2$ as the formula.

2. *Orthonitrophenylacetic acid.* When crystallized from hot water, white needles are obtained, which melt at 137–138°. Analysis gave the following as the composition: $C_6H_4.NO_2.CH_2CO_2H$. When

boiled with potassium permanganate this acid yields orthonitrobenzoic acid. Upon reduction it gives oxindol.

3. *Bromo-derivatives.* Bromophenylacetic acid is prepared by treating phenylacetic acid and mercuric oxide suspended in water, with the calculated quantity of bromine in small quantities, keeping the mixture cool. When the reaction is complete, excess of caustic soda is added, and the filtrate from the mercuric oxide is treated with hydrochloric acid; the bromo-acid separates out as a precipitate, and, after washing, is crystallized from alcohol. These crystals melt at 76°. The alcoholic mother liquors yield an acid with a higher melting point, and give a barium salt from which crystals are obtained, which yield the acid on treatment with hydrochloric acid.

Parabromophenylacetic acid is obtained by crystallizing the above acid from hot water. It melts at 114–115°. It is a monobromophenylacetic acid, with the same melting point as the parabromophenylacetic acid of Loring Jackson and W. Lowery (Ber., **10**, 1210). The formula is $C_8H_7BrO_4$.

Orthobromophenylacetic acid. The mother liquors from the barium salts mentioned above, are treated with lead acetate, and the washed precipitate boiled with dilute sulphuric acid. The filtrate from the lead sulphate gave an acid, in crystals, melting at 103–104°. Its formula is $C_8H_7BrO_2$. It gives orthobromobenzoic acid by oxidation with potassium permanganate; hence, it is orthobromophenylacetic acid.

These results show that the parabromophenylacetic acid described by Radziszewski, melting at 76°, is a mixture of two isomerides.

4. *Bibromo-derivatives.* A bibromo acid is made from crude bromophenylacetic acid (m. pt., 76°), by exposing it to sun-light in sealed tubes, with the calculated quantity of bromine, for several months. The product obtained is converted into methyl ether, as it cannot be obtained in crystals. The methyl ether is distilled under reduced pressure, and comes over at 220–230°; it is saponified, the potassium salt decomposed with hydrochloric acid, and an acid crystallized from water. This acid has a melting point of 114–115°, and a bromine determination shows it to be bibromophenylacetic acid.

5. *Bromonitro-derivatives.* Short notices of two of these have already been published (Ber., **10**, 530 and 1637). The following facts are given, and also an account of a third isomeride.

Parabromometanitrophenylacetic acid, $C_6H_3.NO_2.Br.CH_2CO_2H$, crystallizes from hot water, and melts at 113–114°. It is insoluble in

cold water, but dissolves easily in alcohol and ether. By oxidation with potassium bichromate and sulphuric acid, it gives parabromometanitrobenzoic acid. Its formula is $C_8H_6NO_2BrO_2$. The barium salt has the composition $Ba(C_8H_5BrNO_4)_2 + H_2O$. It is soluble in water, and a dilute solution gives precipitates with silver nitrate, copper acetate and lead acetate.

The methyl ether gives yellowish needles, melting at 40–41°. Its ethyl ether has only been obtained as an oily liquid.

Parabromometamidophenylacetic acid, $C_6H_3.NH_4.Br.CH_2CO_2H$, is obtained by reducing the nitro acid with tin and hydrochloric acid, and crystallizes from water. It is easily soluble in alcohol and chloroform, sparingly in ether. It melts at 133–134°. Its hydrochlorate crystallizes in white needles, soluble in cold water.

Alpha-bromonitrophenylacetic acid crystallizes from water, and melts at 167–169°. It is soluble in alcohol and ether, and insoluble in cold water. The barium salt is soluble in hot water, and has the composition $Ba(C_8H_5BrNO_4)_2 + 4H_2O$. The aqueous solution of the barium salt gives precipitates with silver nitrate, copper acetate, and lead acetate.

The methyl ether forms needles melting at 66–68°; the ethyl ether forms yellowish needles.

Alpha-bromamidophenylacetic acid is made by reducing the nitro acid with tin and hydrochloric acid. It crystallizes in needles which melt at 167°, with decomposition. It is soluble in alcohol and chloroform, sparingly in ether.

Beta-bromonitrophenylacetic acid. This is the third isomeride formed with the two preceding ones. It was obtained by extracting with chloroform the mother liquors from the nitration of bromophenylacetic acid. The extract was dissolved in glacial acetic acid, and slow evaporation gave an acid, melting at 162°, and crystallizable from hot water. Reduction with tin and hydrochloric acid gives bromamidophenylacetic acid, melting at 168°. The formula of the bromamido acid given is $C_6H_3.Br.NH_2.CH_2CO_2H$.

On the Specific Volume of Water of Crystallization, T. E. THORP and JOHN I. WATTS (1880, 102).—Playfair and Joule have noticed that the volumes of certain hydrated salts are exactly equal to that of the water they contain, considered as ice. In salts less highly hydrated, this law does not hold good.

The present paper contains the results of an investigation to determine the precise relation between the specific volume of a salt and its degree of hydration. These results were obtained by taking

the specific gravity of a number of salts of different degrees of hydration. The specific volume of a salt is the volume in cubic centimeters occupied by the equivalent of the salt taken in grms. The following table gives a synopsis of the results obtained by the authors:

Hydrate.	0	1	2	3	4	5	6	7
Copper sulphate.....	44.4	54.3	67.0	80.0	.....	109.1	.....	.....
Magnesium sulphate....	44.8	55.6	67.0	....	.....	112.4	130.8	146.6
Zinc sulphate.....	45.6	54.7	66.6	....	.....	113.7	130.2	146.8
Nickel sulphate.....	44.6	56.5	....	....	.....	.....	129.0	144.6
Cobalt sulphate.....	44.7	55.2	70.9	....	97.4	114.6	130.1	146.0
Manganous sulphate....	45.0	55.7	73.6	86.6	98.2	114.4	.....	.....
Ferrous sulphate.....	44.5	56.2	67.7	....	100.5	.....	.....	146.7
Mean of means.....	44.8	55.5	68.8	83.3	98.7	112.9	130.0	146.1

The numbers at the head of the vertical columns indicate the molecules of water of hydration contained in the salt used, and each result is the mean of experiments by the authors and others; the figures at the foot of the vertical columns being the mean of these means.

The conclusions, drawn from the above observations, are, that the volume occupied by the several molecules of water varies with the degree of hydration. Thus for the first hydrate its mean relative value is 10.7, and the difference between the monohydrate and the dihydrate is 13.3; between the dihydrate and the trihydrate, 14.5; between the trihydrate and the tetrahydrate, 15.4, and so on for other hydrates.

Note on the Formation of Ozone During the Slow Oxidation of Phosphorus, HERBERT MCLEOD (1880, 118).—Ozonised oxygen, prepared with a Siemen's tube, was passed through a U-tube containing sodium carbonate solution, a mixture of potassium bichromate and sulphuric acid, and potassium permanganate saturated with carbonic dioxide. In all the cases the ozone passed through even when the tube was placed in boiling water.

Corresponding experiments were made with air in which phosphorus was slowly oxidizing. After drawing the air through the U-tube with one of the above reagents, both cold and at 100°, in all cases it gave a blue color when passed through potassium iodide and starch solution.

The effect of raising the tubes to 150–200° was also tried, and the gas escaping still decomposed potassium iodide.

Since hydroxyl and ozone may be formed simultaneously by oxidizing phosphorus, the action of these bodies upon one another was examined. Some commercial peroxide of hydrogen was intro-

duced into a cylinder of ozonised oxygen, and the gas affected ozone paper even after prolonged agitation. But if the acid mixed with the hydroxyl is neutralized with sodium carbonate, or the liquid is made very slightly alkaline, the ozone is destroyed.

The author regards the above experiments as evidence that the gas formed by the slow oxidation of phosphorus, has the properties of ozone and not peroxide of hydrogen.

On the Analysis of Organic Bodies Containing Nitrogen, etc., W. H. PERKIN (1880, 121).—After pointing out the defects of the present methods, the author describes a number of experiments to obtain a simple and effective method to attain the point in view, and finally adopts the following:

Instead of using metallic copper to stop the nitrous fumes given off when nitrogenous bodies are burned in oxygen, potassium chromate is used. It is found that this salt absorbs nitrous fumes when cold, and also when heated. It is, of course, essential that the chromate should be free from alkali. The presence of small quantities of bichromate is not harmful; but bichromate alone does not work as well as the chromate. The chromate is granulated by evaporating the solution, and stirring the mass till dry; or pumice stone may be saturated with the solution and dried. With uric acid the author found 6–7 inches of filled tube sufficient. The best temperature appears to be just below a dull red heat.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office**, by ARNO BEHR.

July 6, 1880.

229,518.—*Acid phosphate for baking powders.* CHAS. A. CATLIN.

Seems to claim dicalcic phosphate as a substitute for cream of tartar.

229,573 and 229,574.—*Preparation of potassium phosphate and of sodium phosphate for baking powder.* GEORGE F. WILSON and CHARLES A. CATLIN.

The manner of preparation and the exact nature of these compounds cannot be understood from the claims.

229,586.—*Extracting precious metals from ores.* THOMAS C. CLARK.

The claim is for roasting the ore and dropping it, while hot, in a cold solution containing salt, prussiate of potash and caustic soda.

229,653.—*Process of making whisky.* MARSHALL T. ALLEN and WILLIAM E. BRADLEY.

Proposes to wash out the sugar and starch contained in the "slop," and to use the liquid in a fresh operation in place of water.

229,669.—*Separating graphite from foreign matter.* HUGH BURGESS.

In passing the graphite-bearing mineral between rollers, the mineral is crushed, while the particles of graphite are only flattened. Sifting separates the two materials.

229,697.—*Extract of coffee.* DAVID C. GUE and JOSEPH C. GRANT.

A fluid extract of coffee, consisting of a mixture of a cold infusion of the berry, primarily obtained, with a cooled decoction of the residuum of the infusion.

229,705.—*Pulverulent preparation of phosphoric acid.* EBEN N. HORSFORD.

A solution of phosphoric acid is absorbed in dry starch, and this preparation dried and pulverized. In connection with a dry alkaline carbonate it can be used as a baking powder.

July 13, 1880.

229,817.—*Manufacture of vulcanized india-rubber products.* HENRY GERNER.

A mixture of india-rubber, camphor and flour.

229,924 and 229,925.—*Roofing cement and roofing composition.* TERENCE SPARHAM.

The first named product consists of plumbago, soap-stone and coal-tar, the second of the same ingredients with an addition of mica.

229,928.—*Tanning process.* THOMAS P. TUCKER.

The process consists in the successive treatment of the hides with various liquids of a very complex nature, for the particulars of which the specification must be seen.

July 20, 1880.

230,103.—*Filtering-press.* LEVI L. BAXLEY.

230,106.—*Process for making and purifying sulphate of alumina or alum.* WILLIAM, THOMAS and JAMES CHADWICK and JOSIAH W. KYNASTON.

The object is to remove the iron from the solution of sulphate of alumina. According to claim 2, arsenious acid is added to the solution, which is neutralized with carbonate of lime until the iron is precipitated. The residual arsenic is precipitated with sulphuretted hydrogen.

230,151.—*Porous or spongy mineral composition and non-conductor of heat.* DE WITT C. SANFORD.

A combination of plaster of Paris, bicarbonate of soda and water, to which is added flour, glue, glucose, or paper-pulp.

230,158.—*Machine for testing lubricants.* ROBERT H. THURSTON.

230,171.—*Process of, and apparatus for, treating the residuum from petroleum refineries.* HENRY BOWER.

The process is for the recovery of sulphuric acid from sludge acid, and consists in the washing of the latter with water and in the mechanical separation of the acid solution from oily and carbonaceous matter. The acid solution is concentrated in lead vessels and afterwards distilled. The essential part of the invention seems to be the apparatus used, for description of which the specification must be seen.

230,216.—*Process for manufacturing nitro-derivatives from cellulose, etc.* JULES A. ARNAULT and JULES and CHARLES SCHMERBER.

The materials are treated with nitric acid, in a gaseous state.

230,225.—*Tanning and preparing leather.* SAMUEL BLOOM.

230,239.—*Process and apparatus for distilling petroleum.* SAMUEL CHENEY.

By distilling with live steam under a pressure of 75 pounds, about 20 per cent. of light lubricating oil is recovered from crude heavy oil.

230,303.—*Manufacture of aqua ammonia.* JAMES L. MARSH.

Claims the heating of a mixture of sulphate of ammonia, lime and water, by steam applied to the surface of the containing vessel, and, at the same time, agitating it by means of a horizontal stirrer, to expose the greatest possible area of surface to the heat.

230,369.—*Treating molten copper for making cast hollow cylinders, and other castings.* SAMUEL WALKER.

To the molten metal is added cryolite, either alone or together with borax, or acetate of lead, or both, in order to prevent porosity.

July 27, 1880.

230,398.—*Purifying extracts of bark.* EARNSHAW BRADLEY.

The extract is evaporated to a density of 10° Bé, and then artificially cooled in an apparatus constructed for the purpose. The liquid is conducted through a series of vats, overflowing one into another, where the substances which have been separated on cooling, are allowed to settle.

230,415.—*Phosphated nutritive powder.* SAMUEL W. HALEY.

Milk is precipitated with monobasic phosphoric acid, and the washed and dried curd is mixed with phosphate and bicarbonate of soda, salt and flour.

230,501.—*Apparatus for the recovery of waste sulphuric acid.* AMÉDÉE G. SEBILLOT.

Relates to the treatment of certain ores with sulphuric acid. For particulars, reference must be had to the specification.

230,518.—*Refining cocoa-nut oil.* ALEXANDER P. ASHBOURNE.

Boiling the oil with sugar, eggs and alum.

Foreign Patents.

Condensed from R. BIEDERMANN'S Report to the German Chemical Society, by OTTO H. KRAUSE.

ALFRED NOBEL, Paris: *Apparatus for concentrating sulphuric acid and similar liquids.* (Germ. P., No. 10149, January 15, 1880.)—A tower constructed cast iron pipes, within which a number of porcelain basins are supported, one above another, upon suitable projections. Each basin has a hole through which a glass rod passes and rests upon the one below, thus permitting the acid which enters at the top of the tower, to flow from one basin to another without spattering. When all the basins are filled, the tower is heated by means of the hot air flues which surround it. The acid vapors evolved, as well as the concentrated acid, are drawn off below. The apparatus is based upon the property of cast iron of resisting the action of sulphuric acid *vapor*, and it is claimed that even acids containing nitrogen compounds may be concentrated in it.

H. UNGER, Leipsic: *Improvements in apparatus for the ammoniacal manufacture of soda.* (Germ. P., No. 10392, December 21, 1879.)—The sodium bicarbonate to be calcined is passed through a system of retorts, by means of endless screw conveyers. Suitable arrangements are provided to exclude air. The opening for withdrawing the gases and vapors is so placed that the latter cannot come in contact with and be condensed by the cold bicarbonate entering the apparatus.

T. WASTCHOUK and N. GLOUCHOFF, Moscow: *Preparation of caustic alkalies by electrolysis.* (Germ. P., No. 10039, December 2, 1879.)—The novel feature of this method, already previously attempted, of preparing sodium hydrate from

sodium chloride by electrolysis, consists in an arrangement for removing the gases which tend to polarize the electrodes.

E. CAREY, H. GASKELL and F. HURTER, Widnes: *Purification of alkaline lyes.* (Engl. P., No. 2939, July 18, 1879.)—The inventors remove ferrocyanogen compounds from lyes by exposing them to the air, or by adding sulphur, sulphides or hyposulphites, and heating to 150°. For this purpose the solution is made to circulate through a heated coil of pipes. By employing sodium thiosulphate the following reaction takes place:

$$5Na_2S_2O_3 + Na_4FeCy_6 = 6NaCyS + 2Na_2SO_3 + 2Na_2SO_4 + FeO,$$

or, by employing sodium pentasulphide:

$$6Na_2S_5 + 4Na_4FeCy_6 = 24NaCyS + 2Na_2S + 4FeS.$$

W. P. THOMPSON, Tranmere, Chester: *Manufacture of aluminium, sodium, and allied metals.* (Engl. P., No. 2101, March 27, 1879.)—In this process molten iron alone, or together with hydrogen or carbon, is employed as a reducing agent, and it is proposed to carry out the operation in an apparatus similar to a Bessemer converter. This is to contain two divisions. After the iron has been melted in one of these, it is run into the other by turning the converter. Hydrogen, or carburetted hydrogen, is admitted to this division through one tube, whilst aluminium chloride, or fluoride, in a fused or volatilized state, enter by a second. Hydrogen and ferric chloride are evolved, and aluminium and carbon are said to remain in the converter. The mixture of iron, aluminium and carbon, is passed into the other division, where a current of air consumes the carbon only, leaving an alloy of iron and aluminium.

In the preparation of sodium, the hydrogen is dispensed with. Iron mixed with excess of carbon is heated in the converter with sodium hydrate, and the sodium formed, distilled off. When pure aluminium is required, sodium is first prepared in the manner just described, and aluminium chloride, or fluoride, admitted to the division of the converter containing it, air being excluded.

EMIL ANDRE, Coblenz: *Method of dephosphorizing pig iron.* (Germ. P., No. 9635, March 14, 1879.)—The pig iron direct from the blast furnace is dephosphorized in open pits. These are lined with overburned dolomite, to which 2 per cent. of a mixture of lime and sulphuric acid has been added, as a binding material, and are charged with large pieces of oxides of iron, rich in manganese. Pulverized manganic oxide, preferably mixed with lime, or fluor spar, is added to the molten iron as it runs into the pit, in such proportion, that tribasic salts may be formed with the phosphorus, silicium and sulphur present.

ACTIEN-VEREIN FUER BERGBAU, ETC., Gutehoffnungshuette, Oberhausen: *Method of lining Bessemer converters with bauxite.* (Germ. P., No. 9701, March 17, 1879.)—The bauxite is calcined, ground and mixed with binding materials, such as clay, lime or burned dolomite, and the mixture used as it is, or in the form of bricks.

W. GOEBEL, Hanover: *Gas generator for retort furnaces.* (Germ. P., No. 9367, February 11, 1879.)—The generator is composed of two connected parts: a pit furnace, for producing carbonic acid, and a cylinder, filled with coke, in which the carbonic acid is reduced to carbonic oxide.

AUGUST KLOENNE, Dortmund: *Method of preventing the hydraulic mains of gas furnaces from becoming clogged with thickened tar.* (Germ. P., No. 9965, De-

cember 16, 1879.)—The inventor passes, continuously or periodically, small quantities of cold or hot crude phenols into the main to dissolve the thick mass collecting there.

WILLIAM BELL, New York: *Manufacture of paraffine from cannel coal, peat, etc.* (Engl. P., No. 3011, July 24, 1879.)—The substances mentioned are extracted with naphtha or ether.

C. THOMAS, W. J. FULLER and S. A. KING, Bristol, England. *Improvements in the process of recovering glycerine from soap waters.* (Germ. P., No. 9979, September 30, 1879.)—The soap waters are evaporated until the greater part of the salts separates. The alkalies and alkaline carbonates which still remain in solution are combined with an excess of stearic or oleic acid, forming soap, which separates with the fatty acids upon the surface of the liquid. The fatty acids are syphoned off, the remaining liquid filtered and clarified, and the glycerine obtained by concentrating and distilling. (See also this JOURNAL, **2**, 105.)

VICTOR VON OFENHEIM, Vienna: *Improved method of bleaching ozokerite, ceresine, paraffine, petroleum, stearine, and other hydrocarbons and fatty matters, with the aid of the hydroxides of aluminium, iron, manganese and magnesium, and the silicates of aluminium and magnesium.* (Germ. P., No. 9981, October 24, 1879, being an addition to Germ. P., No. 9291; see this JOURNAL, **2**, 232.)—Besides the substances mentioned in the original patent, the silicates of aluminium and magnesium may be employed for bleaching ozokerite, etc.

ERNEST FARRINGTON, Paris: *Treatment of asphaltum for paving.* (Germ. P., No. 2560, June 26, 1879; see this JOURNAL, **2**, 300.)

JOHN C. MARTIN, Richmond: *Improvement in mills for grinding white lead.* (Germ. P., No. 10209, September 21, 1879.)—The grinding apparatus is covered to prevent the poisonous dust from spreading. An automatic scraper removes the ground material from time to time.

GEO. J. LEWIS, Philadelphia: *Improvements in the manufacture of white lead.* (Germ. P., No. 10061, October 26, 1879.)—The vapors obtained by subliming the ore (galena) are oxidized by a current of hot air. The heat resulting from the burning of the sulphur, permits a saving of fuel.

J. S. GRAWITZ, Paris: *Preparation of aniline black.* (Engl. P., No. 2958, July 21, 1879.)—The inventor cites the following process as an example: To a warmed mixture of 800 parts, by weight, of water, 150 starch, 50 gum, and 70 potassium chloride, are added upon cooling 100 parts aniline, 100 parts hydrochloric acid, sp. gr., 1.16, and 100 parts water; finally, freshly precipitated hydroxide of iron from 200 parts chloride of iron, of sp. gr., 1.175.

THEILIG and CLAUS, Crimmitschau, Saxony: *Improvements in the oxidizing process in dyeing with aniline black.* (Germ. P., No. 9904, November 8, 1879.)—The fabric, impregnated with aniline salt, potassium chlorate, vanadium chloride, etc., is exposed to a current of hot air, to oxidize the aniline. After the material has assumed a certain degree of dryness, vapor of water is mixed with the current of air. To neutralize the liberated acids, ammonia gas may be passed over the fabric, together with the hot air, etc.

GESELLSCHAFT FUER HOLZSTOFFBEREITUNG, Grellingen near Basel. *Method of bleaching wood pulp.* (Germ. P., No. 9922, November 7, 1879.)—The moist pulp is treated with sulphurous acid gas.

J. C. ZIMMERMANN and O. HOLTZWICH, Dresden: *Apparatus for preparing japan and oil varnish.* (Germ. P., No. 9444, July 15, 1879.)—The apparatus for melting the resins is heated by hot air, or superheated steam, to avoid burning the contents. A second apparatus serves for the continuous preparation of varnish from linseed oil. In this, the oil flows in a thin layer over surfaces of lead, whilst a current of hot air from the melting apparatus passes over the oil.

CHEMISCHE FABRIK AUF ACTIEN, successor to E. SCHERING, Berlin: *Method of preparing tannic acid in a form similar to crystalline needles.* (Germ. P., No. 10076, December 10, 1879.)—The solution of tannin is evaporated until it forms a mass, which breaks upon cooling. The warmed mass is allowed to flow through small holes in the bottom of a vessel placed about 15 feet high. The threads so formed are wound upon a rotating drum, and subsequently broken up.

SIMON ULLMO, Lyons: *Rapid tanning process.* (Germ. P., No. 9919, September 12, 1879.)—The hides are treated with a tanning solution, which contains per 100 lbs. of wet hide, 30 lbs. dividivi, 20 lbs. bark of oak-root (*garouille*), 30 lbs. alum, 15 lbs. soured barley meal, and 1 lb. sulphate of copper.

A. CORDS and A. DEININGER, Berlin: *Method of removing and preventing boiler incrustation.* (Germ. P., No. 9185, June 20, 1879.)—The inventors add sulphate of iron to the water; an easily removable mud is said to be formed, and even old incrustations dissolved. (In feed water containing air, a basic salt will be formed, and the sulphuric acid liberated will attack the iron of the boiler, in case a sufficient amount of base is not present in the water to neutralize the acid. R. B.)

KARL DRECHSLER, Dresden: *Pulverulent lubricant for shafting, etc.* (Germ. P., No. 10375, December 17, 1879.)—Mixture of graphite, and white or yolk of egg, applied in the dry state.

KARL F. HARTMANN, Wuestewaltersdorf: *Method of impregnating fabrics with cellulose.* (Germ. P., No. 10080, January 16, 1880.)—Finely divided vegetable fiber, mixed up with potato flour and water, is applied to the goods with the aid of rollers.

W. KETTE, Jassen: *Precipitation of protein bodies from waste waters of potato starch works.* (Germ. P., No. 10033, October 29, 1879.)—The waters from the grated potatoes are precipitated with an acid solution, obtained by boiling waste products containing starch, with sulphuric acid.

E. C. CARRATTE and A. F. D. CLAPARÈDE, Geneva: *Method and apparatus for converting the coagulum of milk into a dry powder.* (Germ. P., No. 9485, October 10, 1878.)—The milk is coagulated by means of cream of tartar or dilute sulphuric acid, and spread upon a sieve, to allow the watery matters to flow away. To every kgrm of the coagulated paste, 2 grms of potassium carbonate, or sodium bi-carbonate, and 100 grms sugar, are added, and the whole mixed, dried and powdered.

G. KUEHNEMANN, Dresden: *Improvements in bread making.* (Germ. P., No. 10019, January 4, 1880, being second additional patent to Germ. P., No. 4611, of March 15, 1878; see this JOURNAL, **1**, 304, 456.)—According to the original patents, the following substances are obtained from grain and bran:

1. Amylo-dextrine, soluble albumen, extractive matters, and salts (grain juice).

2. Pulverulent precipitates composed of starch and albuminoids.

To a 10–15 per cent. solution of the substances mentioned under 1, the powder of starch and albuminoids is added, together with as much flour as is necessary to form dough; finally a little salt, and leaven or yeast.

E. H. HUCH, Dresden: *Method of preserving the blood of cattle.* (Germ. P., No. 10031, October 21, 1879.)—The fresh blood is mixed with pulverized unslaked lime. A gelatinous mass separates easily from the precipitated lime. It is said to be valuable for feeding.

CHARLES ROSS, Teufelsbrueck, near Altona: *Apparatus for filtering liquids containing gases.* (Germ. P., No. 9379, September 16, 1879.)—The whole filtering apparatus is placed under, and maintained at, a constant pressure by the gas contained in the liquid.

C. H. TIFFEN, Hove: *Remedy for tooth-ache and neuralgia.* (Engl. P., No. 2923, July 18, 1879.)

THE AMERICAN CHEMICAL SOCIETY.

XXXVI.—Proceedings.

Regular Meeting, Thursday, September 9th, 1880.

Prof. A. R. Leeds in the chair. Twelve members only being present, no regular business was transacted.

The following paper was read: 1. "On the Effect of Change of Density in Alum Purpurine Solutions on the Absorption Bands," by Prof. Henry Morton.

In the discussion which followed, Prof. Morton said that he had used alum labelled "pure," which contained free sulphate of alumina; the alumina precipitated the purpurine, forming a lake; therefore it was necessary to crystallize the alum to purify it. He also remarked that in using the cylindrical bottle, to concentrate the rays of light on the spectroscope, the bands are displaced towards the red end of the spectrum: In two cases the observations were: 50°26′ and 50°27′, when cold, and 50°20′ and 50°21′, when hot. Prof. Morton remarked, further, that the heat employed in his experiments did not destroy the purpurine.

The Recording Secretary then read the following paper: 2. "On Arita Porcelain," by N. Matsui, Ph.D., Tokio, Japan.* In connection with the analyses given in this paper, Prof. Leeds suggested that the lime should have been incorporated with the results of the calculations for feldspar, as it is almost always present in these minerals.

After which the minutes of the meeting of the Board of Directors, held Sept. 8th, 1880, were read; also the report of the Committee, on the informal meeting held in Boston.

After which the meeting adjourned.

ARTHUR H. ELLIOTT,
Recording Secretary.

* See this Journal, **2**, 315.

XXXVII.—On the Effect of Change of Density in Alum Purpurine Solutions on the Absorption Bands.

(Abstract of a Paper read before the American Chemical Society, Sept. 9th, 1880.)

By Henry Morton, Ph.D.

The phenomenon noticed in this paper was the displacement of the maxima of absorption in solutions of purpurine in alum-water.

1st. With changes in amount of alum.

2d. With changes in temperature.

3d. With change in the alum salt used, *i. e.*, ammonia, potash or soda alum, or sulphate of alumina.

The character of these changes was as follows:

Greater amount of "alum" in the solution carried the maxima downwards in the spectrum.

A higher temperature likewise had the same effect, as also had a greater molecular weight in the alum salt employed.

These results are in remarkable accordance with those noticed by the writer in the salts of uranium.*

Abstracts from American and Foreign Journals.

Bulletin de la Société Chimique de Paris.

Abstractor, E. H. S. Bailey, Ph.B.

On Persulphuric Acid; its Formation by Electrolysis, Berthelot (**33**, 242).—A further study of this acid, discovered in 1878 by the author. It is formed by electrolysis by placing dilute sulphuric acid in a porous vessel, which in turn is surrounded by another vessel containing the same liquid. The whole is kept cool by a serpentine coil, through which water flows. Platinum electrodes are employed, and a current from 6 or 9 Bunsen cells. The persulphuric acid is formed at the positive pole. Water passes through the porous cup more rapidly than the acid. At a later stage of the operation, as the acid becomes more concentrated, and hence presents greater resistance, it seems to be acted upon by the electric current, forming hydric peroxide. The fact that this latter gradually disappears may probably be accounted for by the well-known action of concentrated sulphuric acid upon it.

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* See *Chemical News*, **28**, 47, 113, 164, 233, 244, 257, 268.

On the Heat of Formation of Persulphuric Acid, BERTHELOT (**33**, 246).—The heat of formation is measured by diluting the liquids obtained by electrolysis with 15 or 20 volumes of water, and treating them successively with a solution of iodide of potassium, and sulphurous acid. A check experiment, made under the same conditions by mixing solutions of iodide of potassium and sulphuric acid of corresponding strength, furnishes data for the complete explanation of the reaction: S_2O_7 (dilute) + SO_2 (dilute) + $3HO = 3(SO_3HO)$ (dilute). The heat of formation is found to be 13.8 cal.

The formation of hydric peroxide, of persulphuric acid and of ozone, constitutes a gradual series, thus:

Ozone	$O + O = (O_2)$ absorbs	14.8 cal.
Persulphuric Acid	$S_2O_6 + O = (S_2O_7)$ absorbs	13.8 cal.
Hydric Peroxide	$HO + O = (HO_2)$ absorbs	10.8 cal

These three bodies are mutually transformable into each other in accordance with certain relations that the author has developed. All contain active oxygen in a condition to be readily given up to oxidizable bodies.

On a new Sulphocyanate of Platinum, VINCENTE MARCANO (**33**, 250).—By mixing bichloride of platinum and sulphocyanate of potassium, it is possible to obtain, upon cooling, crystals having a composition corresponding to the formula: $\left.\begin{matrix}Cy_8\\Pt\end{matrix}\right\}S_8 + 2H_2O$; the reaction can be expressed thus:

$$8\left(\left.\begin{matrix}Cy\\K\end{matrix}\right\}S\right) + 3PtCl_4 = \left.\begin{matrix}Cy_8\\Pt\end{matrix}\right\}S_8 + PtCl_2 + 8KCl.$$

The crystals belong to the monoclinic system. The angle of the oblique rhomboidal prism measures 114°25′; inclination of axes 80°46′. This body is a new proof of the octatomicity of platinum.

Reactions of Tetrachloride of Titanium, Stannic Chloride and Antimonic Chloride upon Acetic Acid and Acetic Anhydride, A. BERTRAND (**33**, 252).—Messrs. Friedel and Ladenburg (*Ann. de Chim. et de Phys.*, [4 series,] **27**, 428) have made a mixed silico-acetic anhydride, by acting upon chloride of silicon with crystallizable acetic acid, or with acetic anhydride. The author notices that tetrachloride of titanium, stannic chloride and antimonic chloride have the same action as chloride of silicon with crystallizable acetic acid; hydrochloric acid is formed, but with the anhydride, chloride of acetyl.

On Inactive Glucose, or Neutral Sugar, U. GAYON (**33**, 253).—In discussing the results obtained by M. Horsin-Déon (reviewed in this JOURNAL, **I**, 488) the author claims to have arrived at similar results earlier, and by a different method.

1st. Neutral and inverted sugar have the same composition.

2d. The formation of neutral sugar precedes that of inverted sugar.

From the results of experiments, the presence of inactive glucose in raw sugar and molasses can be accounted for. All raw sugars contain a variety of organisms capable of secreting an inverting ferment, which develops with the greatest rapidity in those sugars containing the most coloring and organic matter. Heat and moisture favor their multiplication, and the transformation of the sugar. Inactive glucose is at first formed when the organisms multiply very rapidly; sometimes the inactive glucose is mixed with a little true inverted sugar.

On Neutral Sugar and Inverted Sugar, P. HORSIN-DÉON (**33**, 256).—A review of the results arrived at by different experimenters when sugar is inverted; the first form that it takes is that of neutral sugar. The sugar remains neutral if the inversion has taken place in the presence of a little moisture, but it becomes levogyric, taking the rotary power of normal inverted sugar, when considerable water is present.

Action of Bromine upon Epichlorhydrine, E. GRIMAUX and P. ADAM (**33**, 257).—Bromine readily attacks epichlorhydrine at 100°. By cooling the product of the reaction a crystalline mass separates from a heavy oil. The crystals consist of hydrate of tribromochloracetone, which is readily dehydrated on exposure to air and becomes $C_3H_2ClBr_3O$, a colorless oily liquid. The heavy oil which separates from the crystals above mentioned appears to be chlorobromhydrine. The reaction which takes place is similar to that of bromine upon dichlorhydrine. A substitution product is at first formed, and the hydrobromic acid produced unites with epichlorhydrine changing it to chlorobromohydrine, which is in turn attacked by bromine. The reaction is—

$$\underset{\text{Epichlorhydrine.}}{2(C_3H_5ClO)} + Br_6 = \underset{\text{Tribromochloracetone.}}{C_3H_2Br_3ClO} + \underset{\text{Chlorobromhydrine.}}{C_3H_6ClBrO} + 2HBr.$$

On the Determination of Glycerine in Wine, HIP. RAYNAUD (**33**, 259).

Synthesis of Ulmic Bodies, A. MILLOT (**33**, 262).—By passing an electric current through a dilute ammoniacal solution, using for the positive pole a plate of gas carbon, some of the carbon is dissolved producing a black coloration, and this black coloring matter is precipitated by a mineral acid. This is soluble in water, especially if warm, but is precipitated by alcohol. Although containing nitrogen it gives off no ammonia upon boiling with potassic hydrate. The precipitate produced by HCl, dried at 150°, has the composition:

$$C = 54.75\ ;\ H = 4.00\ ;\ N = 12.40\ ;\ O = 28.85.$$

If a caustic potash solution is used instead of ammonia, a similar substance is obtained, except that it is free from nitrogen.

Action of Ammonia upon Anthraquinonesulphonic Acid, R. BOURCART (**33**, 263).—A discussion of the properties of amidoanthraquinone, in regard to the "*action of ammonia upon β-anthraquinonedisulphonic acid.*" It is ascertained that if the sodium salt be treated at 180°, with aqua ammonia in sealed tubes, a substance is produced which is precipitated in whitish flakes when the solution is neutralized. The acid has the formula:

$$C_6H_3(SO_3H)\begin{matrix}CO\\CO\end{matrix}C_6H_2(NH_2)(OH).$$

The ammonia salt, which crystallizes from dilute alcohol, has the symbol: $C_6H_3(SO_3NH_4)\begin{matrix}CO\\CO\end{matrix}C_6H_2(NH_2)(OH) + 2\frac{1}{2}H_2O$.

On the Decomposition of Hydric Peroxide in the Presence of Alkalies, and on the Derivatives of Baric Binoxide, BERTHELOT (**33**, 289).—M. Schöne (*Annalen der Chemie u. Pharm.*, **192**, 257, 1878) has discovered that there are definite combinations of baric binoxide and hydric peroxide; the author has measured the heat of formation of the different compounds. In regard to the decomposition of hydric peroxide in the presence of an alkali, the theory advanced is that a certain proportion of the former unites at first with the alkali, heat being disengaged: $2HO_2 + BaOHO = BaO_3HO_2 + 2HO$. This compound is then changed into hydrate of the binoxide, and loses half of its oxygen, heat being again disengaged: $BaO_2HO_2 = BaO_2HO + O$. The hydrate of the binoxide in turn becomes hydrate of protoxide, its excess of oxygen being displaced by water, and more heat being evolved: $BaO_2HO = BaOHO + O$. Another portion of hydric peroxide is then attacked, and so on, till it is entirely decomposed.

Analysis of the Waters of the Bourboule, ED. WILLM (**33**, 292).—Waters from different sources were analyzed. It is a noteworthy fact that the arsenic is nearly all found in the soluble part of

the residue, from which it is inferred that it exists in the form of an alkaline arseniate. The quantity of trisodic arseniate varies from 5.1 to 17.2 mgrms per liter. Bicarbonate of lithium is also present in quantities from 37.9 to 44.3 mgrms per liter.

On the Action of Bromine upon Diphenylmethane, C. FRIEDEL and M. BALSOHN (**33**, 337).—The object of these investigations is to ascertain whether bromine can be substituted in the place of the hydrogen of the non-aromatic part of the radical. By acting upon one molecule of diphenylmethane with two molecules of bromine under appropriate conditions, bibromo-diphenylmethane may be formed. This when heated with water is decomposed into benzophenone and hydrobromic acid. If one molecule of bromine is used instead of two, monobromodiphenylmethane is formed. The alcoholic solution of the latter acted upon by alcoholic potassa forms mixed ethylbenzohydrolic ether. By treating with amylic alcohol instead of ethylic, and potash, amylbenzohydrolic ether is produced, or if potassic acetate and acetic acid are used we obtain acetate of benzohydrole. Benzohydrolic ether and benzohydrole can also be made from the monobromodiphenylmethane.

On the Constitution of the Salts of Rosaniline and of Analogous Coloring Matters, A. ROSENSTIEHL (**33**, 342).

On a Continuous Method for the Preparation of Acetic Ether, J. A. PABST (**33**, 350).—Acetic ether can be made by a process similar to that employed for the manufacture of sulphuric ether. The mixture of alcohol, sulphuric acid and acetic acid which is in the apparatus, gives off at first a little sulphuric ether, but afterwards at 130°–135°, acetic ether of 85%. This is washed with a saturated solution of chloride of calcium, dried over chloride of calcium, and redistilled.

Berichte der Deutschen Chemischen Gesellschaft.

Abstractor, H. ENDEMANN, Ph.D.

Phenyllactic Acids, EMIL ERLENMEYER (**13**, 303).

Phenylbromlactic Acid, EMIL ERLENMEYER (**13**, 305).

Orthonitrobenzaldehyde and its Behavior towards Nascent Hydrogen, CH. RUDOLPH.—Tin and glacial acetic acid produce with orthonitrobenzaldehyde a substance of basic character, C_7H_5N. The same, with tin and hydrochloric acid, produces C_7H_4ClN. The same reaction was to be employed for other orthonitroaldehydes, the authors intending to first submit the aldehydes of orthonitro-

phenylacetic and orthophenylglyoxylic acids in the hope of obtaining indol and indigo. The already mentioned publications of Baeyer and Jackson have, however, been the cause that the author has desisted from further work in this direction.

Amides and Anilides of β-oxybutyric Acid, L. BALBIANO (**13**, 312).

Phenanthrenedisulphonic Acid and some of its Derivatives, EUGEN FISCHER (**13**, 314).—One part of phenanthrene is gradually added to four parts of pyrosulphuric acid of commerce, and, after a good mixture is obtained, the whole is heated from ¼ to ½ hour on the water bath. For the purpose of purification, the lead salt is prepared, and this decomposed by H_2S.

The barium salt contains 28.96 per cent. of barium, which corresponds to the formula $C_{14}H_8.(SO_3)_2.Ba$.

The author has used his material to study a series of reactions: Melting with alkalies, heating with acetyl chloride, potassium cyanide and yellow prussiate of potash, after dehydration, and likewise sodium formate. The investigations are however not sufficiently advanced for publication.

A Series of New Dyestuffs, EUGEN FISCHER (**13**, 317).—Phenanthrene disulphonic acid, when heated with phenols, especially resorcine, produces beautifully colored substances. In this reaction one molecule disulphonic acid and two molecules of resorcine participate; a condensation takes place, water being given off, and a product is formed, possessing a formula analogous to resorcinephthaleine. The analytical results differ, in part, considerably from the calculated composition, and the author therefore assumes that as yet he has not obtained a product free from by-products produced in the reaction.

Phenol disulphonic acid gives with phenols a similar reaction; the product is likewise highly colored.

On Isophthalophenone, E. ADOR (**13**, 320).

On the Action of Carbonic Oxide upon Alkalic Hydrates at Higher Temperatures, A. ZENTHER.—The author, owing to a publication in this JOURNAL (**13**, 23), calls attention to the fact that he has published during the previous summer a treatise upon the action of the substances given in the title, as likewise the action of carbonic oxide upon mixtures of

Sodium methylate and sodium acetate,
Sodium ethylate and sodium acetate,
Sodium ethylate and sodium valerate,
Sodium amylate and sodium valerate.

These were printed in *Jena's Zeitschrift fuer Naturwissenschaft*, Supplement to Vol. XIII.

Since then, the author has examined the action of carbonic oxide upon mixtures of

Sodium amylate and sodium acetate,
Sodium phenylate and sodium acetate,
Sodium phenylate and sodium carbonate,
Sodium ethylate and sodium carbonate,
Sodium ethylate and sodium benzoate,
Sodium ethylate and sodium phenylacetate,
Sodium phenylate and potassium oxalate,
Sodium ethylate and potassium oxalate,
Sodium ethylate and sodium succinate,

and also the action of carbonic oxide upon sodium ethylate and sodium cinnamate. The investigation will be continued, and will embrace the action upon polybasic alcohols.

The Synthetic Preparation of Formic Acid, O. LOEW (**13**, 324).—The author, owing to a publication in this JOURNAL (**13**, 23), calls attention to a reaction published by him in 1864. Carbon bisulphide and water, with iron filings in excess, heated to 100° for some time in a sealed tube, produced iron sulphide, iron formate, carbon dioxide and also two more substances of more complicated composition.

Identification and Determination of Chlorine in the Presence of Bromine and Iodine, G. VORTMANN.—Bromine and iodine may be driven off by boiling a solution of the salts to be tested for chlorine, with lead peroxide and acetic acid. They pass off mainly as bromine and iodine; a small portion, however, is converted into bromic and iodic acids, which remain with the lead peroxide added in excess. After filtration the solution may be tested for chlorine. The reaction is reliable enough for quantitative determinations.

Cinnamic Aldehyde obtained by the Pancreatic Digestion of Fibrine, J. OSSIKOVSZKY (**13**, 326).

On the Constitution of Tyrosine and Skatole, J. OSSIKOVSZKY (**13**, 328).

On the Velocity of Reactions, B. PAWLEWSKI.—The author finds that using the same acid with barium, strontium and calcium carbonate, the velocity of the reaction is in inverse proportion to the atomic weight of the metal contained in the carbonate.

Vanilline in certain Unrefined Beet Sugars, C. SCHEIBLER (**13**, 335).

Some Dichromates, K. PREIS and B. RAYMAN (**13**, 340).—The author describes in this paper the barium, strontium and lead dichromates.

On the Action of Iodine upon Aromatic Compounds with long Side Chains, B. RAYMAN and K. PREIS (**13**, 344).—Iodine, acting upon cymole, produces a series of hydrocarbons which commence to boil below 100°, the boiling pt. gradually rising to 300°. The hydrocarbons produced are the same as those produced by the action of iodine upon oil of turpentine. The hypothesis that oil of turpentine produces under the influence of iodine first cymole, seems therefore in part at least verified.

Iodine acting upon camphor produces the same hydrocarbons.

On the Oxidation of Sulphaminemetatoluic Acid, IRA REMSEN (**13**, 347).—Treats of the reliability of Lassaigne's reaction for nitrogen, which consists in the melting of the substance to be tested with sodium, and testing a solution obtained from the melt, with iron salts, which in the presence of nitrogen will produce a blue precipitate. The author defends Lassaigne's method against the objections raised by Jacobsen.

On the Splitting up of Inactive Malic Acid, G. J. W. BREMER (**13**, 351).—The separation of the two acids, which act upon polarized light, from the inactive acid obtained by the action of HI upon racemic acid, was attained by the preparation of the cinchonine salts. The cinchonine salt of the acid, which turns the plane of polarization to the left, is precipitated, while the other salt remains in solution.

Dinitronaphthalene, F. BEILSTEIN and A. KURBATOW (**13**, 353).—α-dinitronaphthalene, heated with nitric acid, 1.15 specific gravity, to 150° C. in a sealed tube, gave nitrophthalic acid, dinitrobenzoic acid and some picric acid; while the β-compound gave dinitrophthalic acid, dinitrobenzoic acid and some picric acid. A description of dinitrophthalic acid follows.

On Dinitrobenzoic Acid, F. BEILSTEIN and A. KURBATOW (**13**, 355).—The dinitrobenzoic acid obtained in the reactions of the preceding paper is, as determined by the properties of its ethyl ether, the well-known modification.

Action of Dehydrating Substances upon Acids, B. VANGEL (**13**, 355).

On the Condensation of Benzohydrole and Naphthalene, A. LEHNE (**13**, 358).

On Cubic Alum and the Accommodation of Chrome Alums, A. POLIS (**13**, 360).—In order to produce cubic crystals of alum, which remain clear, the author adds soda to the alum solution instead of, as has formerly been done, potash or ammonia; chrome alum could only then be obtained in cubes, when an alumina alum cube, prepared by the first described method, was allowed to grow in a chrome alum solution. A series of other crystallizations, made under varying conditions, follows.

On Gluten, TH. WEYL and BISCHOFF (**13**, 367).—According to the authors, gluten is not originally contained in the flour, but is produced from a substance called vegetable myosine by the action of a ferment. The investigation will be continued.

Contributions to the Knowledge of Daturine, ERNST SCHMIDT (**13**, 370).—The author maintains the identity of daturine and atropine, by a direct comparison of the daturines and atropines from different manufacturers, and prepared by himself from the plants.

Artificial formation of Tropaic Acid, A. LADENBURG and L. RÜGHEIMER (**13**, 373).—Hydrotropaic acid on oxidation by means of potassium permanganate, yielded the atrolactinic acid of Fittig and Wurster. The latter acid was converted into atropaic acid on distillation with dilute hydrochloric acid. Tropaic acid was obtained by reduction of the chloroatropaic acid produced by the addition of hypochlorous acid to the above atropaic acid. The authors assign to atrolactinic acid and tropaic acid the following formulæ:

$C_6H_5C.CH_3.OH.COOH$ = atrolactinic acid.

$C_6H_5CH.CH_2OH.COOH$ = tropaic acid.

Upon Daturine, A. LADENBURG and G. MEYER (**13**, 380).—The authors conclude that daturine, hyoscyamine and duboisine are identical.

Aromatic Amide Acids, FERD. TIEMANN (**13**, 381).—Benzaldehydecyanhydrine, on digestion with alcoholic ammonia at 60–80°, in sealed vessels, yields benzamidocyanide, which on decomposition by means of dilute hydrochloric acid, yields phenylamidoacetic acid. This acid is identical with the phenylamidoacetic acid of Stoeckenius (*Berl. Ber.*, **11**, 2002) obtained in the reaction of phenylbromoacetic acid and ammonia.

Diphenyl Derivatives, containing Sulphur, S. GABRIEL and A. DEUTSCH (**13**, 386).—Derivatives of diphenylmonosulphonic acid.

Some Experiments upon the Vapor Densities of the Alkali Metals, VICTOR MEYER (**13**, 391).—The vapor density of sodium cannot be determined in glass, porcelain, silver or platinum vessels, as the vapor or the metal acts upon these materials. The author expects to repeat his experiments in vessels made of graphite.

Behavior of Iodine at High Temperatures, VICTOR MEYER (**13**, 394).—The experiments were performed both in glass, porcelain, and in platinum vessels. The following results were obtained: The density of iodine at 600° corresponds to the formula I_2; at 800° a marked decrease becomes observable. The density is constant between 1027—1567°, corresponding exactly to the value calculated for $\frac{2}{3}I_2$.

Contribution to the Knowledge of Chlorine, V. MEYER and H. ZÜBLIN (**13**, 339).—The authors find the vapor density of free chlorine gas to correspond to the value calculated for Cl_2, while nascent chlorine, according to previous experiments, corresponds to $\frac{2}{3}Cl_2$ (*Berl. Ber.*, **12**, 1430).

Some Observations on Vapor Densities, V. MEYER (**13**, 401).

Platinic Bromide, V. MEYER and H. ZÜBLIN (**13**, 404).

Density of Bromine Vapor at Yellow Heat, V. MEYER and H. ZÜBLIN (**13**, 405).—The vapor density of nascent bromine from platinic bromide was found to correspond to $\frac{2}{3}Br_2$.

Calorimetric Determination of Temperature, V. MEYER (**13**, 407).

Potassium Indigo-white-sulphate and Indoxylsulphate, E. BAUMANN and FERD. TIEMANN (**13**, 408).—The authors give a series of reactions which prove that the two substances, mentioned in the title, differ sufficiently to justify the position which the authors have taken against Baeyer, who doubts the existence of potassium indoxylsulphate.

Fittica's Fourth Nitrophenole, S. NATANSON (**13**, 415).—The author has been unable to obtain this substance by following Fittica's method, and concludes that this substance, the existence of which would not be possible according to Kekulé's theory, does actually not exist. Fittica stated that it was fluid at ordinary temperature; boiling point, 190°.

Contribution to the Constitution of Phthalylchloride, E. VON GERICHTEN (**13**, 417).—Not suitable for abstraction.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office,** by ARNO BEHR.

Aug. 3, 1880.

330,646.—*Closing drums containing caustic soda.* FREDERICK H. MORT.

The cover of the drum is provided with internal projections, which are held firmly by the solidified soda, and thus secure the cover to the drum.

230,753.—*Fabrication of onyx from agate.* CARL P. CULLMANN and CARL A. LORENZ.

Immersing one side in a bath of dilute nitric acid and iron, the other side in a bath of carbonate of potassa and water, then drying the stones on a stove and then burning them.

230,841.—*Tanning compound.* SIMON ULLMO.

For 100 lbs. of skins, 30 lbs. divi-divi, 30 lbs. garouille or oak-bark, 30 lbs. alum, 14 lbs. sour barley-flour, 1 lb. sulphate of copper.

Aug. 10, 1880.

230,872.—*Solution for nickel plating.* HARRY L. HAAS.

Formate of nickel with excess of acid.

230,874.—*Pulverulent preparation of phosphoric acid.* EBEN N. HORSFORD.

The solution of phosphoric acid and monocalcic phosphate, resulting from the action of sulphuric acid on bone-ash is, after concentration, mixed with starch, thoroughly dried and pulverized. This preparation, mixed with a dry alkaline carbonate, can be used as a baking powder.

230,878.—*Insulating compound.* ADOLPHUS A. KNUDSON and FREDERICK L. KANE.

Asphaltum mixed with paraffine oil, petroleum residuum or candle tar.

230,898.—*Paint oil from petroleum acid residues.* ANDREW G. SHADE and GEORGE H. MOORE.

230,903.—*Incrustation preventive.* JOHN B. SOWASH and GARDNER V. WRIGHT.

Chloride of ammonium, sweet oil, lard oil, Virginia black oil or residuum of petroleum and sugar.

230,912.—*Roofing compound.* PHILEMON WRIGHT.

A mixture of the "flyings" of ground calcined gypsum and coal tar.

230,919.—*Compound for water proofing and preserving building materials.* ROBERT M. CAFFALL.

Consists of creosote, 1 lb.; turpentine, 5 lbs., and paraffine, 25 lbs.

230,965.—*Enameling compound.* GEO. RUSSELL.

Consists of asphaltum, naphtha, shellac, protoxide of lead and boiled linseed oil.

230,991.—*Process of obtaining the glutinous and starchy substances from Indian corn.* LEWIS T. BENNETT.

Consists in a mechanical separation of the hulls and germs from the starchy portions of the corn.

231,035.—*Tannin extract.* PAUL GONDOLO.

The material containing tannin is extracted with slightly acidulated water, the free acid neutralized by an alkali, and the extract then clarified by the addition of blood and the application of heat.

231,064.—*Electro-deposition of aluminum and gold alloy.* GEORGE LINSENMAYER.

231,106.—*Preparing moss for upholstery.* CHARLES M. SARTWELL.

Treating the moss with lime-water.

Aug. 17, 1880.

231,328.—*Process of rectifying spirits.* CASPER KALTHOFF.

Before redistillation a small quantity of nitrate of silver is dissolved in the crude alcohol.

231,335.—*Filter.* JOHANN KRO[illegible]G.

A new filter press.

Aug. 24, 1880.

231,419.—*Process for preserving wood.* JONAS D. FRANCKS.

The process consists in saturating the wood with a mixture of lime-water and urine in a heated state.

231,484.—*Process for the conversion of marine plants into pulp.* EDOUARD V. T. L. GORGES.

The plants are macerated in caustic lye, after draining plunged into dilute sulphuric acid, and the resulting pulp finally washed in an alkaline bath.

231,489.—*Obtaining tannic acid.* JULIUS HOLTZ.

Brief: The acid is obtained in acidular form, at a low temperature, by forcing the evaporated extract through a perforated floor into a heated chamber, in which a partial vacuum is formed.

231,532.—*Process of uniting wrought and cast iron.* MORGAN BURNS.

That part of the wrought iron object around which the fluid iron is to be cast, is coated with a mixture of kerosene oil and chalk.

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That part of the wrought iron object around which the fluid iron is to be cast, is coated with a mixture of kerosene oil and chalk.

231,540.—*Lining gas generators, acid chambers and fountains for mineral waters.* JOHN COLLINS.

The coating to be applied consists of a mixture of asphaltum, benzine and plumbago.

231,563.—*Manufacture of iron.* ROBERT H. HAMILTON and WILLIAM GRIFFITH.

In the puddling process there is mixed into the molten metal a certain proportion of borax or of a mixture of borax with black oxide of manganese, sal-soda or common salt, and nitrate of soda.

231,583.—*Insulating Compound.* WILLIAM W. JAQUES.

Rubber, beeswax and Venice turpentine.

August 31, 1880.

Composition for flavoring cigars. HENRY K. REISS.

New England rum, alcohol, oil of apple, tonka beans, valerian root and laudanum.

231,737.—*Lactometer.* GEORGE TANNER.

A number of tubes and scale, combined on a stand so that the amount of cream separated can be easily measured.

231,804.—*Process of economically obtaining starch and glucose from corn.* HENRY C. HUMPHREY.

Proposes to use the residue from the manufacture of starch for the production of glucose.

231,807.—*Process of preserving meat in the carcass.* RICHARD JONES.

Consists in introducing the preservative solution into the circulatory organs of the animal, after insensibility has been produced, and before the heart has ceased to beat.

231,841.—*Acid siphon pump.* ELLEN AUGUSTA NICHOLS, WOLCOTT B. MANWARING and OLIN L. LIVESEY.

231,858.—*Process for the manufacture of cement.* ERNEST SOLVAY.

By calcining together chloride of calcium and clay, a soft silico-aluminate of lime is produced. This is intimately mixed with lime, and then constitutes the cement.

231,860.—*Manufacture of chloride of lime.* ERNEST SOLVAY.

Hydrate of lime is formed into small fragments of agglomerated morsels, by which the complete absorption of the chlorine is effected.

Sept. 7, 1880.

231,909.—*Incrustation preventive.* FULTON HENDERSON.

A mixture of 8 lbs. of coal tar, 8 ounces of red lead and 1 ounce of linseed oil.

232,051.—*Method of purifying rancid butter.* JAMES CHESTON MORRIS.

Uses a solution of boracic acid.

232,071.—*Process of treating spirituous liquors.* ADDISON M. SAWYER.

For the purpose of aging such liquors, air is forced through them which is "charged with the fumes of quick-lime."

Sept. 14, 1880.

232,110.—*Preparation of magnesia and the manufacture of refractory bricks therefrom.* ALFRED BRACONNIER.

Calcined dolomite is treated with a solution of chloride of ammonium, which dissolves the lime.

Sept. 21, 1880.

232,381.—*Explosive compound.* MAX TSCHIRNER.

A mixture of picric acid and chlorate of potassium.

Sept. 28, 1880.

232,615.—*Solution for nickel plating.* CHARLES G. PENDLETON.

A solution of acetate of nickel containing an excess of acetic acid.

232,685.—*Recovering sulphuric acid from sludge acid.* EDWARD CLARK.

232,755.—*Solution for the electro-deposition of nickel.* JOSEPH H. POTTS.

A solution of the acetates of nickel and of lime containing free acetic acid.

Foreign Patents.

Condensed from R. BIEDERMANN'S Report to the German Chemical Society, by OTTO H. KRAUSE.

F. PECHINEY, Salindres: *Recovery of sulphur from alkali waste.* (Engl. P., No. 3194, August 8, 1879.)—The yellow liquors from alkali waste are oxidized by passing a current of air through them, as has often been done before. The inventor proposes, however, to interrupt the injection of air when all the calcium monosulphide has been oxidized and before calcium sulphite has been formed. Calcium thiosulphate and polysulphide are obtained from which, upon the addition of acids, all the sulphur is precipitated and not partly evolved in the form of sulphurous acid, as is the case with lyes which have been completely oxidized.

S. G. THOMAS: *Manufacture of phosphates from slag.* (Engl. P., No. 3196, August 9, 1879.)—The slag resulting from Thomas' process of dephosphorizing iron contains 15—20 per cent. of phosphoric acid. It is pulverized and treated with hydrochloric acid. The filtered solution is oxidized with chlorine or manganic peroxide to obtain ferric phosphate, which is then precipitated from a boiling solution by lime or dolomite. The precipitated ferric phosphate is heated with sodic sulphate and coal. Air is admitted toward the end of the operation in

order to burn away the sulphur, leaving ferric oxide and trisodic phosphate. The latter is dissolved in water, and lime added, whereby calcium phosphate and sodium hydrate are obtained. (See also this JOURNAL, **2**, 300.)

MORITZ FREYTAG, Bonn: *Absorption of sulphuric acid contained in gases from zinc, lead or copper furnaces.* (Germ. P., No. 9969, November 26, 1879.)—The gases enter the lower part of a tower filled with coke or stones, through which sulphuric acid trickles.

ALEX. MUELLER, Berlin: *Method of disinfecting and purifying waste waters.* (Germ. P., No. 9792, December 11, 1878.)—The waters previously freed from metallic salts and antiseptic substances and neutralized by lime, are run into large basins and kept at a temperature of 25–40° C. Fermentation is then induced by adding substances which favor the production of bacteria or other ferment organisms, in order to decompose the organic matters.

JOSEPH SCHMIDLIN, Hyde: *Printing with aniline black.* (Engl. P., No. 3161, August 6, 1879.)—The inventor adds to the mixture of aniline salt and potassium chlorate, an *insoluble* chromate and a per-salt of iron, to enable him to print alizarine red and other aniline reds together with black upon fabrics.

EUGEN STUTZER, Berlin: *Manufacture of shoddy wool.* (Germ. P., No. 10122, October 19, 1879.)—Vegetable fibre from jute, hemp, flax, etc., is treated successively with caustic lye at 175°, and ammoniacal sulphate of copper and caustic soda, then washed, dried and mixed with wool.

HERMANN KRUPP, Vienna: *Method of obtaining a firmer coating of silver upon metals.* (Germ. P., No. 9976, January 21, 1879.)—The objects are first nickel plated, then passed through a copper bath and finally silver plated with the battery.

NIC. STENZEL, Prague, and L. BROZ, Rokcyan: *Method of applying the enamel composition to the inner surface of moulds.* (Germ. P., No. 9921, July 12, 1879.)—The mould is first coated with plumbago and then the composition suspended in water applied evenly. (See this JOURNAL, **2**, 141.)

J. M. A. DEHERRYPON, Paris: *Method of dehardening glass.* (Germ. P., No. 9950, September 23, 1879.)—Glass hardened by rapid cooling is dehardened by heating and slowly cooling it in suitably constructed ovens.

A. W. KLINGHAMMER, Braunschweig: *Apparatus for extracting substances systematically by means of warm liquids of low boiling points.* (Germ. P., No. 9826, March 30, 1879.)—A system of suitably placed vessels for warming the solvents and for condensing the vapors from the extracted liquid, and for determining the gravity of the distillate.

E. C. LABOIS and L. L. LABOIS, Paris: *Apparatus for making bisulphide of carbon and sulphuric acid from iron and copper pyrites.* (Germ. P., No. 10561, November 2, 1879.)—Relates to the combination of a vertical retort with a pyrites furnace. The retort is charged with pyrites and charcoal, and part of the sulphur distilled off as carbon disulphide. After a certain time the charge is transferred to the roasting furnace, and the rest of the sulphur obtained as sulphurous acid, which is passed into lead chambers.

W. F. NAST, Paris: *Apparatus for obtaining ammonia from manure and urine.* (Germ. P., No. 10704, January 11, 1880.)—The substances are brought together with milk of lime into a boiler which can be rotated upon its axis. Superheated steam is admitted, and the ammonia evolved is washed and absorbed by an acid.

F. BRIEGLEB, Heufeld: *Apparatus for dividing a current of liquid into a number of streams of equal volume, which can be run off separately.* (Germ. P., No. 10386, November 15, 1879.)—Consists of a cone with radial projections, and is intended to replace the Barker's mill for distributing the sulphuric acid in Gay Lussac and Glover towers.

GEO. AARLAND, Stollberg, near Aix la Chapelle: *Method of decomposing sulphides of the alkaline earths with calcium chloride.* (Germ. P., No. 10486, December 24, 1879).—Substitution of calcium for magnesium chloride in Schaffner-Helbig's process for regenerating sulphur from alkali waste.

R. HASENCLEVER, Aix la Chapelle: *Preparation of bisulphite of lime with the air of gases from fires or from pyrites furnaces.* (Germ. P., No. 10710, December 9, 1879.)—Milk of lime trickling through a tower is brought into contact with the sulphurous gases from which sulphuric acid has been previously removed.

K. & TH. MOELLER, Kupferhammer, near Brackwede: *Method of purifying waste waters containing arsenic.* (Germ. P., No. 10462, February 25, 1879.)—Waste waters containing the sulphur compounds of calcium and arsenic (from tanneries) are purified by a series of precipitations with hydrochloric acid, or with carbonic acid from flue gases, and with hydrate of lime.

THE AMERICAN CHEMICAL SOCIETY.

XXXVIII.—Proceedings.

Regular Meeting, Thursday, October 7th, 1880.

Dr. E. R. Squibb in the chair.

In absence of a quorum at the regular hour, business proceedings were deferred, and the following paper was read: "On the Constitution of Ultramarine," by H. Endemann, Ph.D.

In the discussion which followed the reading of this paper, Dr. Leeds remarked that he had a difficulty in conceiving the oxidation of the sodium sulphite to sodium sulphate, under the influence of heat alone. Dr. Endemann replied that it was a fact that sodium sulphate was always formed. Dr. Behr said that he did not understand Dr. Endemann's explanation of the conversion of white into green ultramarine, and further remarked that in organic chemistry, dehydration (etherification) does not produce colored bodies, and that it was strange that green should be found, under these circumstances; Dr. Endemann did consider the process as one of dehydration, but also one of oxidation. Dr. Alsberg remarked that it was strange that the darkest ultramarine contained the most silica, and yet, according to Dr. Endemann, this silica was not necessary to the formation of the color. Dr. Endemann said that this color nucleus may contain silicon in the place of alumina, as he had explained in the reading of his paper.

There now being a quorum, the minutes of the meetings held June 3d and September 9th, 1880, were read, and approved.

Minutes of the meeting of the Board of Directors, held September 8th and September 29th, 1880, were read. After which the following gentlemen were unanimously elected:

As members:

C. H. Torrey, School of Mines, Columbia College, N. Y. City.
G. T. Bihn, 523 Tasker st., Philadelphia, Pa.
Dr. Karl Stahl, N. W. Fertilizing Co., Union Stock Yards, Chicago, Ill.
Hermann Poole, Practical School, Buffalo, N. Y.

And as associate members:

J. R. Savage, manufacturing chemist, Philadelphia, Pa.
Thomas Harrison, manufacturing chemist, Philadelphia, Pa.

After which the following gentlemen were nominated:

As members:

ALBERT C. HALE, State School of Mines, Golden, Colorado.
NARCISSE PIGEON, 128th st. and 4th ave., N. Y. City.
THEODORE LUNGWITZ, Jersey City, N. J.
BYRON N. WITTMAN, Chemist, Reading, Pa.
HENRY J. SEAMAN, Crane Iron Co., Catasaugua, Pa.
CHAS. W. SCHMICH, Rockhill Iron & Coal Co., Orbisonia, Huntington Co., Pa.
Dr. HENRY FRIEDBURG.

As associate members:

HERMANN T. VULTE.
F. G. WIECHMANN, School of Mines, Columbia Coll., N. Y. City.
T. D. O'CONNOR, School of Mines, Columbia Coll., N. Y. City.
CHARLES KYTE, Jr., 3 East India Ave., London, E. C., England.

After which it was—

Resolved, That the members present nominate three members to serve on a committee for the selection of officers for the coming year, and that the three members receiving the highest number of votes shall constitute such a committee.

The votes being counted, the following gentlemen were found to have the highest number of votes: Dr. A. R. LEEDS, Mr CASAMAJOR, Dr. E. R. SQUIBB.

It was further—

Resolved, that this committee shall carry out the same plan as was followed last year in the selection of officers.

After which the resignations of the following gentlemen were read, and accepted: E. L. YOUMANS, E. SCHROEDER, JOHN P. MARSHALL.

The following papers by Prof. H. W. WILEY, of Lafayette, Indiana, were read by title, and referred to Committee on Papers and Publications:

1. "The Rotatory Power of Commercial Glucose and Grape Sugar. A Method of Determining the Amount of Reducing Substances present, by the Polariscope."

2. "The Effect of Heating with dilute Acids, and treating with Animal Charcoal, on the Rotary Power of Glucose."

After which meeting adjourned.

ARTHUR H. ELLIOTT,
Recording Secretary.

XXXIX.—On the Constitution of Ultramarine.

By H. Endemann, Ph.D.

The delay which has occurred in the publication of the Journal of the American Chemical Society, coupled with the facts that the article, as originally written, has been published already in the *Chemical News*, and that Mr. Carl Heumann has attacked these views in the *Chemische Industrie*, makes it desirable that I should enlarge it with respect to some points, while it may bear condensation in others. The paper, as originally written, pretended merely to give my views regarding the constitution of ultramarines with sufficient facts to convey my ideas to those who have made the study of ultramarine a specialty, leaving closer scrutiny to their own efforts.

I shall adhere to this plan now, but since Mr. Heumann has not only attempted to pervert my own writings, but also to call his own perversions absurd, I see myself compelled to put certain points more prominently before the readers. My views regarding the constitution of ultramarine were first formed in 1877, and in order to prove their correctness I made it my task to prepare compounds, which should unmistakably prove the existence and possibility of those bodies which I consider to be the cause of the unusual composition of ultramarine.

I commenced with the aluminium sulphides prepared by various methods, and being there unsuccessful for reasons readily understood by those who have tried to work with these substances, introduced one more metal into the reaction.

These experiments are not concluded. In 1879 I had to discontinue my work, and with the view of discontinuing it entirely, I published at last my views in 1880, working the subject out sufficiently to bear publication, by using the advances in our knowledge reached meanwhile by others, as far as they were accessible to me.

Many have been the attempts to account for the peculiar and high color of ultramarine. Some authors have looked upon certain impurities as the actual bearers of the color (iron sulphide), others speak of a blue modification of sulphur, and others again of silicium and aluminium sulphide in very fine dissemination throughout the mass, but without chemical combination with the balance of the constituents. Lately, apparently, it has become a matter of taste to abandon entirely the discussion of the derivation of color. The statement is made that this question cannot be decided, that it is impossible, for

instance, to state why certain salts of cobalt are red and certain salts of copper blue. Nobody has attempted to decide why certain copper salts are blue, but it must be acknowledged that in dealing with certain compounds of copper of blue color, constitutional peculiarities may be readily recognized in all of them, by which they may be easily distinguished from other salts of copper which are colorless. The color of the salt in doubtful cases is a very positive indicator with regard to the type from which the constitutional formula should be derived.

Heumann reasons in a similar manner (*Ann. Chem.*, **203**, 207). He says: "Nobody enquires into the coloring principle of Prussian blue, though neither iron nor cyanogen are blue, and, as nitrogen and oxygen may unite to form the reddish-brown nitrogen dioxide, we may accept that the combination of a silicate with a sulphide may possess a blue color. The desire to define the coloring principle of ultramarine is, therefore, it is to be hoped, a question which hereafter will not be asked." Mr. Heumann seems here entirely to forget that he has failed to show how a sulphide may combine with a silicate.

Having this problem in view, the following propositions have been made:

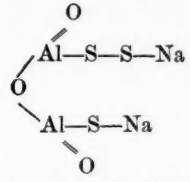
We are justified in insisting upon and foretelling for a colored compound an unusual grouping of the atoms, if its constituents, under the hitherto accepted arrangement of the atoms, would produce only colorless compounds.

If, in ultramarine, we consider the proportion of aluminium, silicium and sodium, to the non-metallic constituents, oxygen and sulphur, we find an excess of the latter.

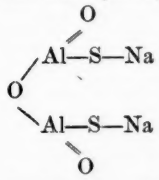
Aluminium is regarded as a tetratomic element. All ordinary aluminium compounds are assumed to contain two aluminium atoms linked together by two of their atomicities, leaving six atomicities for combination with other elements. There is a possibility of the existence of compounds without this binding of two atoms by one atomicity,—a possibility that compounds derived from the, as yet unknown, compounds AlO_2 and Al_2O_4, may be prepared.

Considering the composition of ultramarine blue, we find that it consists of silica, soda, alumina, sodium monosulphide, and sulphur, the latter also in chemical combination, as it cannot be removed by solvents unless these at the same time act chemically. Most authors consider it as being united with sodium sulphide, forming polysulphurets. These substances, forming ultramarine, I do not, how-

ever, consider as serving all the same purpose. To simplify the explanation, I propose for the present to regard one portion of the soda and alumina and the whole of the silica, merely as a vehicle necessary for the preparation and existence of ultramarine, as they serve to facilitate the reactions in the first instance, while later in the process they may act in protecting the product against too powerful oxidation. This silicate may have a varying composition, and for this reason alone it would be difficult to correctly ascertain its quantitative relation to what may be called the *color nucleus*, i. e., *the last group on the constitution of which the color of the ultramarine depends.* This we can suppose in ordinary ultramarine blue to be:



and in Heumann's ultramarine blue (*Liebig's Annalen*, **203**, 190):

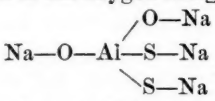


The first of the two, under the influence of acid, will give two-thirds of the sulphur as such, while one-third will be obtained as H_2S. The latter (Heumann's) will give half as sulphur and half as H_2S.

While, therefore, Heumann's ultramarine blue must be considered the purest, we see that ordinary ultramarine blue may contain more sulphur in chemical combination. How much sulphur may thus be added greatly depends upon the process of manufacturing the ultramarine, as I will show hereafter. A substance may therefore be a good blue, and yet analysis will give no fixed relations between the *a* and *b* sulphur, as mixtures of ultramarine rich and poor in sulphur may exist, and many analyses, which have been not generally accepted as correct, should not be rejected, provided the method of analysis which has been used, allows safe deductions to be made.

I. *Ultramarine White.*—The mother substance in the manufacture of blue ultramarine is ultramarine white. To it, as it is white, I assign a constitution analogous to that of the neutral sodium silicate,

a portion equal to half of the oxygen being substituted by sulphur.

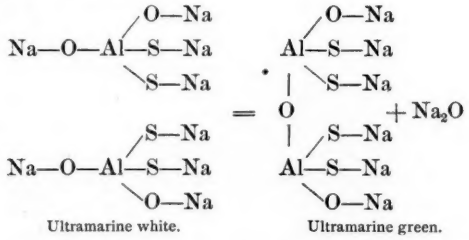


In giving this formula and all the others, I chose them merely as an illustration of the general principle involved in the discussion, and to enable me to convey my ideas, but not as absolute facts. The constitutional formula includes the possibility of partial substitution of aluminium by silicon. That, however, such a substitution takes place to any considerable extent is out of the question, since it would require a color nucleus containing no sodium, which according to our present knowledge of ultramarine is not possible. In the formation of ultramarine white, the presence of the large quantity of sulphur and soda appears as the cause of the breaking of the bond between the two aluminium atoms in alumina. Two molecules of this substance, acted upon by acids and water, will yield 1 sulphur and $3H_2S$, which corresponds with the best ultramarine white yet prepared (Ritter). Most ultramarine whites yield by the action of aqueous acids more free sulphur, but it will be readily seen that the above formula allows a ready interpolation of furthur sulphur atoms. Dry hydrochloric gas acting upon two molecules of ultramarine white produced directly ultramarine blue, chloride of sodium, water and sulphuretted hydrogen.

$$Al_2Na_8O_4S_4 + 6HCl = Al_2Na_3S_2O_3 + 6NaCl + H_2O + 2H_2S.$$

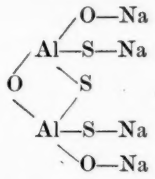
By the action of sulphurous acid gas, ultramarine white is first converted into ultramarine green, two atoms grouping together under loss of Na_2O, forming the first colored compound :

II. *Ultramarine Green:*



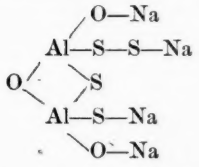
Ultramarine white. Ultramarine green.

which then, by the action of oxygen, which forms sodium sulphate, under further loss of Na_2S, passes into the likewise green compound:



Aqueous acids, with the first green, would produce $3H_2S$ to S, and with the second green, $2H_2S$ to S. It is well known that ultramarine green contains rarely, if ever, the sulphur in such distribution; but this is easily explained by the assumption that these are derived from a white containing interpolated sulphur.

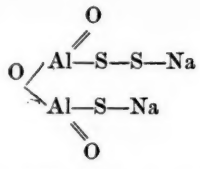
It is even possible that by the combined action of oxygen and sulphurous acid, an interpolated green may be obtained, the sulphur for the sulphate being then furnished by the sulphurous acid, so that in this case sodium alone is removed, leaving:



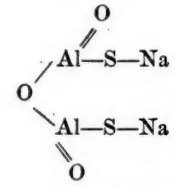
which compound, with aqueous acids, would yield $2H_2S+S_2$.

Gaseous dry HCl would produce all of these compounds, sodium chloride, and H_2S, leaving the blue on treatment with water in the insoluble residue, but this gas has perhaps rarely been used free from air and moisture, and the consequence has been that the reaction is generally accompanied by secondary ones. One of these would be that the mass would not lose so much in sulphur as is indicated by the above stated reaction. Another is indicated by the presence of aluminium chloride in the wash water, which is no doubt produced by water which is formed by the action of air on the hydrochloric gas. In the formation of blue from white directly, water is one of the products of the reaction, and in this case the formation of aluminium chloride is therefore unavoidable, and this substance is, therefore, a regular concomitant of the reaction.

III. *Ultramarine Blue* is, in the manufacture, produced by the action of sulphurous acid and oxygen on the green. Thereby more sodium is removed, and the middle sulphur interpolated in one of the groups ending with Na. The sodium is converted into sulphate. The action of chlorine will produce the same product, leaving:



This product should yield with aqueous acids $H_2S + S_2$. Hydrochloric acid gas would form $H_2S.2NaCl$, and



which latter substance, with aqueous acids, would yield $H_2S + S$.

This is Heumann's ultramarine blue, which in this degree of purity has only once been prepared, owing undoubtedly to the superior care used by Heumann in the production of this compound.

As regards the silicate rest, I will quote here an analysis, made about three years ago for the American Ultramarine Works, which gave the following results:

		Atomic Weight.	Atomic Relation.
SiO_2 ..... 39.28	:	60.0	0.655
Al_2O_3 ..... 26.41	:	102.8	0.257
Na_2O 20.83	:	62.0	0.336
S 12.98	:	32.0	0.406

The sulphur being in two forms, two-thirds being obtained as S while one-third was obtained as H_2S, we divide 0.406 by 3, which gives 0.135 = 1 atom of sulphur. For $S_3 = 0.406$ we require $Na_2O = 0.135$, and $Al_2O_3 = 0.135$ for the color nucleus. This leaves for the silicate:

Na_2O	0.201
Al_2O_3	0.122
SiO_2	0.655

or about $3Al_2O_3.5Na_2O.16SiO_2$.

The complex character of this formula shows the difficulty which we would encounter in introducing the silicate rest into the formula.

Heumann found for this purest ultramarine the following formula: $2Na_2Al_2Si_2O_8 + Na_2S_2$, which, written according to my view, would be

$$\begin{matrix} 2\ Si_2O_4 & & Al_2O_3 \\ Al_2O_3S & & 2\ Na_2O \\ & & Na_2S \end{matrix}$$

Proportion of Oxygen + Sulphur in

Acids.		Bases.
2	:	1

In the above formula, $2Si_2O_4.Al_2O_3.2Na_2O$ represents what I have called the silicate rest, while $Al_2O_3S.Na_2S$ is the so called color nucleus, which, when introduced into the composition of a silicate, will produce a colored compound, even if it be not colored itself.

Since the question of the constitution of ultramarine resolves itself mainly into the determination of the position of the sulphur atoms, my action in considering a certain part of the molecule separately may be justified.

NEW YORK, March 14th, 1881.

XL.—THE ROTATORY POWER OF COMMERCIAL GLUCOSE AND GRAPE SUGAR. A METHOD OF DETERMINING THE AMOUNT OF REDUCING SUBSTANCE PRESENT, BY THE POLARISCOPE.

BY Prof. H. W. WILEY.

In "the trade" the name of grape sugar is applied only to the solid product obtained from corn starch. On the other hand, the term "glucose" is given to the thick syrup made from the same material.

I shall use these words in their commercial sense.

INSTRUMENTS EMPLOYED.

I used in the following investigations two polariscopes, made by Franz Schmidt and Haensch, Berlin. The readings of these instruments, after correction for displacement, agreed well together.

The one was the instrument ordinarily used, in which the purple ray is employed, and the quartz half moons give blue and red tints.

Both of these instruments are graduated to read 100 divisions, each equal to 1 per cent. sugar with a solution containing 26.048 grms pure cane sugar in 100 c.c. In addition to this scale the half shadow has another which gives the actual angular rotation.

This is especially convenient when the specific rotatory power of a substance is to be determined. The angular rotation, however, can be calculated for the former instrument.

For if we take the specific rotatory power of cane sugar at 73.8°, we have the following equation: $73.8 = \frac{\alpha \times 100}{2 \times 26.048}$ whence $\alpha = 38°.45$.

Each division on the cane sugar scale is therefore equal to 0°.3845 angular measure.

This quantity corresponds to the transition tint. It is different for the differently colored rays. In the half shadow polariscope, an instrument particularly adapted to persons afflicted with any degree of color-blindness, the mono-chromatic light coming from the sodium-Bunsen lamp passes through a crystal of acid potassium chromate. The ray thus produced is less rotatable than the "transition tint."

When the instrument gives 100 divisions on the sugar scale, it shows an angular rotation of only $34°42' = 34°.7$. Our division, therefore, of the sugar scale, is equal to 0°.347 angular measure.

To determine the specific rotatory power of cane sugar for the sodium-acid potassium chromate ray, we use the following equation:

$$\text{Sp. rot. pr.} = \frac{34°.7 \times 100}{2 \times 26.048} = 66°.6.$$

To determine the specific rotatory power for any other substance which has been determined for the transition tint, we multiply by the factor 0.9024.

Thus, if we take the specific rotatory power for any other substance which has been determined for the transition tint, we multiply by the factor 0.9024.

Thus, if we take the specific rotatory power of dextrine for the transition tint at 139°, for the half shadow tint it will be, $139° \times 0.9024 = 125°.4$.

These data rest upon the accepted formula :

$$(1)\ \theta = \frac{\alpha}{\varepsilon . \delta . \lambda}$$

$$(2)\ \theta = \frac{\alpha \times \mathrm{v}}{\lambda \times \mathrm{w}}$$

Here α = angular rotation.

θ = specific rotatory power,

ε = amount of substance in one grm of the solution.

δ = specific gravity of solution.

λ = length of observation tube.

w = weight of substance in grms.

MATERIAL.

The glucose studied in the following examinations, was made by the Peoria Grape Sugar Company. I am under obligations to Mr. Allen, the superintendent, for many favors in connection with my work. The grape sugars were made in Buffalo.

ROTATORY POWER.

The average value of θ for the "half shadow ray" is nearly 85°. For the purple ray it is nearly 94°. It, however, varies extremely in different samples.

The following table will show the range of these variations.

TABLE I.

Showing variations of θ in different specimens of glucose and grape sugar, together with the specific gravities of the same.

No.	θ	Sp. Gr.	No.	θ	Sp. Gr.
1	91.50	1.406	11	89.36	1.416
2	91.50	1.407	12	87.73	1.422
3	98.10	1.440	13	89.77	1.417
4	79.93	1.414	14	70.84	1.463
5	75.47	1.414	15	69.40	1.463
6	83.97	1.417	16	87.67	1.412
7	82.75	1.416	17	109.99	1.427
8	86.41	1.415	18	93.17	1.431
9	84.11	1.416	19	89.75	1.409
10	87.19	1.417	20	91.31	1.421

From a study of this table it is seen that within small limits θ is independent of the specific gravity of the solution. Nos. 14 and 15 were grape sugar, and the specific gravity is much higher here than in the glucose, while the value of θ is much less.

Where the increase in density, however, is considerable, as in 3 and 17, there is also a marked increase in the value of θ, although this increase is not proportional to the increment of specific gravity. In masses of homogeneous nature and structure we should expect *a priori* that θ would always be proportional to the density of the body, *i. e.*, to the amount of optically active matter in a unit number of grammes.

It is thus seen without further argument that commercial glucoses are not optically homogeneous, even when made in the same factory and by processes which do not sensibly vary.

A further study of these optical reactions convinced me that the rotatory power of commercial glucose increased as the percentage of reducing substance diminished.

The following table shows the value of θ and the corresponding percentage of reducing matter as obtained by Fehling's solution.

TABLE II.

No.	θ	% Glucose	No.	θ	% Glucose
1	91.50	53.20	11	89.63	53.50
2	91.50	52.36	12	87.73	56.49
3	98.10	54.60	13	89.77	52.36
4	79.93	61.73	14	70.84	69.93
5	75.47	62.50	15	69.40	69.30
6	83.97	59.35	16	87.67	56.34
7	82.75	61.40	17	109.99	39.22
8	86.41	58.80	18	93.17	57.14
9	84.11	58.55	19	89.75	54.37
10	89.19	55.60	20	91.31	56.81

It will be seen by the above table that as the per cent. of reducing matter increases, the value of θ diminishes, and *vice versa.* Nos. 14 and 17 show extreme cases of this law. Nos. 3, 18 and 20, because of their high specific gravities, should not be included in the above generalization. Having thus established the law that the per cent. of reducing matter is in general inversely as the value of θ, it is next proposed to investigate the relation between these two quantities, and determine whether it is constant or variable.

From Nos. 1 and 2, of table II, it is seen that for a value of $\theta = 91.50$, the percentage of reducing matter is 52.78. Let us say for convenience in calculation that $\theta = 91.50$ corresponds to reducing substance = 53 per cent. Let us consider next, some of the cases in which the value of θ differs widely from 91.50. No. 17 of above table affords an example.

The difference is, 109.99—91.50 = 18.49. The difference in the per cent. of reducing substance is 53—39.22 = 13.78. Thus an excess of the value of θ of 18.49 corresponds to a deficit of 13.78 in the percentage of reducing matter.

Therefore a variation of each degree in the value of θ is equivalent to 0.745 in the percentage of a reducing matter. By similar calculations with the other data furnished by the table, I have found, not including Nos. 3, 18 and 20, marked by the high specific gravity, that this number lies between 75 and 78.

I will give the calculation for the first of these numbers, and compare them with the numbers obtained by analysis.

TABLE III.

No.	Variation of Θ	% Glucose by 0.75 Factor.	% Glucose by Fehling's Sol.
1	0.00	53.00	53.20
2	0.00	53.00	52.36
3	—12.08	62.06	61.73
4	—16.03	65.03	62.50
5	— 7.53	58.64	59.35
6	— 8.75	59.57	61.40
7	— 5.07	56.81	58.80
8	— 7.44	58.58	58.55
9	— 4.30	56.21	56.60
10	— 2.14	54.62	53.50
11	— 3.77	55.82	56.49
12	— 1.73	54.29	56.18
13	—20.66	58.32	69.93
14	—22.10	69.56	69.30
15	— 3.83	55.88	56.09
16	+18.49	39.14	39.22
17	— 1.75	54.32	54.05
18	— 0.19	53.14	56.81
19	+ 6.60	47.15	54.60
20	+ 1.66	51.75	57.14

In the above table, Nos. 18, 19 and 20 are the three specimens with high specific gravity. We will, therefore, exclude them from the discussion. In the other numbers the percentage of reducing matter, as calculated from the reading of the polariscope, falls short of the amount obtained by the alkaline copper test ten times, and by an average of 1.018. It exceeds that amount seven times, with an average of 0.75. We thus see that the polariscope will enable us to compute the reducing matter present in a glucose with a probable error of less than one per cent. This is quite accurate enough for practical purposes.

Perhaps a larger number of determinations should be made before constructing a formula for determining the amount of reducing substance in a "straight" glucose. The following formulæ, however, are given provisionally, subject to some slight correction deived from more extended data.

We may have three cases:

1st. The value of $\theta = 91.50$
2d. " " " " < 91.50
3d. " " " " > 91.50

In the first case the percentage of reducing substance in a glucose, if not far from 1.410 sp. gr., will be nearly 53.

In the second case the required percentage may be found by the following formula, in which a = difference between the value of θ and 91.50, and g = per cent. reducing required—

$$g = 53 + 0.75\ a \text{ or } 0.78\ a.$$

In the third case we have

$$g = 53 - 0.75\ a \text{ or } 0.78\ a.$$

In order to make the principle of more general application, I have modified the calculations so as to apply the formula directly to the cane sugar scale of the instrument.

To this end, for instruments using 26.048 grammes for 100 divisions, it is convenient to use only 10 grms of the glucose. If 26.048 grms are employed, the neutral point is thrown entirely beyond the limit of the scale. Ten grammes is the quantity which has been employed in the following table.

The average reading of the sugar scale for ten grammes is about 50.

In the following table will be found the results of the experiments.

TABLE IV.

No.	Scale.	% Reducing Substance by Calculation.	% Same by Cu. test.	Difference.
1	52.65	53.43	53.20	+0.23
2	52.65	53.43	52.36	+1.07
3	46.07	61.66	61.73	−0.07
4	43.05	64.90	62.50	+2.40
5	48.04	58.75	59.35	−0.60
6	47.70	59.63	61.40	−1.77
7	49.80	57.00	58.80	−1.80
8	48.45	58.56	58.55	+0.01
9	50.26	56.45	55.60	+0.85
10	51.50	54.88	53.50	+1.30
11	50.57	56.04	56.49	−0.45
12	51.74	54.58	56.18	−1.60
13	40.83	68.21	69.93	−1.72
14	40.00	69.25	69.80	−0.05
15	50.53	56.09	56.34	−0.27
16	63.80	39.50	39.22	+0.28
17	51.73	54.37	54.05	+0.32
18	52.63	53.46	56.81	
19	56.53	48.59	54.60	
20	53.70	52.10	57.14	

The above calculations were made from the following data.

Starting with Nos. 1 and 2, and discarding small fractions, we find that 53 divisions of the cane sugar scale correspond to 53 per cent. of reducing matter nearly.

By a method of calculation entirely similar to that employed in determining the reducing matter from the fluctuations of θ, I have found that a variation of one degree in the sugar scale corresponds to an inverse variation of nearly 1.25 per cent. of reducing substance.

We may have as in the previous calculation three cases.

1st. The reading of the scale $= 53$
2d. " " " " > 53
3d. " " " " < 53

In the first case $53 = 58$ per cent. nearly.

In the second case, placing a for the reading of the scale, we have

$$g = 53 - (a - 53)\ 1.25$$

In the third case we have

$$g = 53 + (53 - a)\ 1.25$$

In seven of the first seventeen cases the percentage of reducing substance calculated by the above formula, exceeded that given by the copper test, and by a mean amount of 0.539.

In ten of them it fell short, and by a mean amount of 0.938. This method, therefore, can be relied upon to give results which do not vary from the copper test except by a small amount.

Not much more in the way of accuracy can be claimed for the copper test itself.

In Nos. 18, 19 and 20 we have again the cases where the high specific gravities vitiate the results of the calculation.

CORRECTION FOR SPECIFIC GRAVITY.

I next proceeded to find out a method for correcting the reading of the polariscope for variations, caused by changes in the specific gravity of the specimens. First I determined the percentage of water in glucose of different specific gravities ; following are the results:

I.

Sp. gr.	=	1.440
Weight taken	=	5.515, in Pt. dish.
Loss	=	0.35, at 170°, 2 hours.
% H_2O	=	$0.35 \div 5.515 = 6.37$.

II.

Sp. gr.	=	1.431
Weight taken	=	5.86
Loss	=	0.53, 170°, 2 hours.
% H_2O	=	$0.53 \div 5.86 = 9.05$

III.

Sp. gr.	=	1.409
Weight taken	=	4.038
Loss	=	0.622, 170°, 3 hours.
% H_2O	=	15.40

IV.

Sp. gr.	=	1.416
Weight taken	=	4.425
Loss	=	0.525, 170°, 2 hours.
% H_2O	=	11.93

V.

Sp. gr.	=	1.417
Weight taken	=	8.639
Loss	=	1.091, 170°, 3 hours.
% H_2O	=	12.70

VI.

SOLID GRAPE SUGAR.

Sp. gr.	=	1.463
Weight taken	=	7.215, 170°, 3 hours.
Loss	=	0.61
% H_2O	=	9.29

These data are scarcely sufficient to establish a rule for correction for variations in specific gravity, but it appears from them that the formulæ will not vary much from the following:

The rule, 53 divisions = 53 per cent., seems applicable to samples in which the percentage of H_2O is 12 to 14, and of which the sp. gr. is from 1.409 to 1.414. For each variation of 0.001 in the specific gravity, the percentage of H_2O varies about 0.3.

Thus if we take the two extreme cases, viz.: 6.37 and 15.14 per cent. of H_2O, we find the corresponding specific gravities to be 1.440 and 1.409, a difference of 0.031.

The difference in the percentage of water is 9.03. The quotient of $0.0903 \div 0.031 = 3$ nearly.

Let us apply these data to the correction of Nos. 18, 19 and 20 in table IV. I give below these numbers and also their corrections

TABLE V.

No.	Scale.	% Reducing Substance by Calculation.	Same Corrected	Same by Cu. Sol.
18	52.63	53.46	55.83	56.81
19	56.53	48.59	55.17	54.60
20	53.70	52.10	56.55	51.14

The above corrections were based on the supposition that 53 divisions of the scale correspond to 53 per cent. reducing matter, when the sp. gr. = 1.409, and the percentage of water 15.

We may therefore construct the following provisional formulæ for estimating the correction to be applied to the reading of the scale when the sp. gr. of the specimen varies much from 1.409.

Let a = reading of scale.
" a' = corrected reading.
" ε = sp. gr. of the sample.

Then $a' = a - 3a(\varepsilon - 1.409)$, when the sp. gr. is greater than 1.409, and $a' = a + 3a(1.409 - \varepsilon)$, when ε is less than 1.409.

I next propose to undertake some investigations to show the nature and number of the optically active principles present in glucose.

XLI.—THE EFFECT OF HEATING WITH DILUTE ACIDS AND TREATING WITH ANIMAL CHARCOAL, ON THE ROTATORY POWER OF GLUCOSE; WITH NOTES ON THE ESTIMATION OF CANE SUGAR AND GLUCOSE IN MIXTURE.

BY PROF. H. W. WILEY.

Shaking dilute solutions of glucose or grape sugar with animal charcoal produces a slimy precipitate.

I use the words *glucose* and *grape sugar* in their commercial sense. By *glucose* I mean the thick syrup made from corn starch, and by *grape sugar* the solid product made from the same substance; by pure glucose I mean the substance present capable of reducing the alkaline copper solution. I will not take time here to discuss the propriety of these names nor the exact nature of the substances present. I have made some experiments to determine the effect of animal charcoal on the rotatory power of glucose of commerce.

Following are some of the results obtained.

In each case 10 grms of the substance were taken and made up to 100 c.c. The observation tube was 200 m.m. in length.

EXPERIMENTS.

I.

Reading before addition of coal	52°.00
After shaking with 20 grms coal	47°.20
Loss	4°.80

II.

Reading before	52°.63
After adding 10 grms coal	50°.28
Loss	2°.35

III.

Reading before	52°.63
After addition 4 grms ivory black	52°.38
Loss	0°.25

IV.

Reading before	52°.20
After addition 4 grms ivory black	51°.13
Loss	1°.07

V.

Reading before	52°.20
After addition 10 grms ivory black	48°.13
Loss	4°.07

From these figures it is certain that a glucose may lose nearly 10 per cent. of its rotatory power when shaken with animal charcoal. This is a matter of great importance when attempts are made to examine commercial syrups with the polariscope.

These syrups are usually highly colored, and require a great deal of bone black and lead acetate to make them fit for polariscopic examination. I have not yet tried the action of lead acetate on the rotatory power of glucose.

HEATING WITH DILUTE ACIDS.

The following readings as well as those in the preceding part of this paper are divisions on the cane sugar scale.

I

A glucose gave direct reading	53°.70
Heated to 68° with 10 per cent. of its volume of strong hydrochloric acid, reading	52°.96
Loss	0°.74

II.

Heated same glucose for 50 minutes at 68°, reading	50°.76
Loss	2°.94

III.

Direct reading another glucose	43°.36
Heated for 10 minutes at 68°, with 10 per cent. of its volume strong HCl, reading	43°.02
Loss	0°.34

IV.

Heated same glucose 20 minutes at 68°, reading	42°.36
Loss	1°.00

V.

Heated same for 30 minutes at 68°, reading	40°.16
Loss	2°.86

VI.

Heated same for one hour at 68°, reading	39°.26
Loss	4°.10
The percentage of reducing substance in the above s ımple before heating with the acid was	62.50
After	65.58
Increase	3.08

Thus a loss of 4.10 on the cane sugar scale corresponded to a gain of 3.08 per cent. in reducing power.

VII.

A grape sugar gave direct reading	40°.83
Heated with one-fifth its volume strong HCl, for 20 minutes at 68°, reading	31°.70
Loss	9°.13

VIII.

A grape sugar gave direct reading	40°.00
After heating with one-fifth volume HCl for 15 minutes at 68°, gave reading	32°.52
Loss	7°.48

The percentage of reducing substance in the above was:

Before heating	69.30
After heating	71.50
Gain	2.20

Thus a loss of 7.48 divisions in rotatory power corresponded only to an increase of 2.20 per cent. in reducing power.

It will be seen by inspection of the foregoing numbers that glucose and grape sugar undergo quite a degree of change when subjected to the process of inversion as it is practiced on cane sugar. This change is sufficiently great to introduce an appreciable error into the process of estimating cane sugar and glucose in mixtures.

CONVERSION OF THE WHOLE OF THE OPTICALLY ACTIVE SUBSTANCES IN GLUCOSE INTO PURE MONO-ROTATORY GLUCOSE.

I next made an attempt to convert the whole of the optically active substances present in glucose, into pure glucose, by prolonged heating with dilute sulphuric acid.

The conversions were made in a flask fitted with a glass tube about one meter in length. By this device, vapors arising are condensed and flow back into the flask. Thus no loss of volume takes place.

The flask was at first heated in a water bath at 100°. The conversion, however, took place so slowly by this method, that I afterwards added enough salt to the bath to raise the temperature to 104°.

The sulphuric acid employed was of 1.25 sp. gr., and was used in the proportion of 10 per cent. of the volume of the glucose solution.

The readings were made in a tube longer by one-tenth than half the length of the 200 m.m., and the result multiplied by 2.

The following table contains the results of my work.

Nos. 1, 2 and 3 were heated at 100°. No. 1 for 6 hours, No. 2 for 4 hours, and No. 3 for 3 hours.

Nos. 4, 5 and 6 were heated for 3 hours at 102°.

Nos. 7, 8, 9, 10, 11 and 12 were heated for 3 hours at 104°.

TABLE I.

No.	Reading before heating	% Glucose before heating	Reading after heating	% Glucose after heating
1	52.65	53.20	25.92	81.30
2	48.40	59.35	27.14	80.00
3	48.45	58.55	26.10	80.00
4	43.50	62.50	24.72	79.00
5	50.26	55.60	24.18	82.00
6	51.50	53.50	25.38	81.14
7	52.65	52.36	25.89	83.33
8	56.53	54.60	27.36	90.10
9	51.74	52.36	26.19	82.00
10	47.70	61.40	25.36	82.64
11	49.80	58.80	26.02	84.00
12	40.83	69.93	26.07	84.80

In all cases the samples assumed a decidedly yellowish tint before the completion of the operation, interfering somewhat with the delicacy of the final readings.

No. 8 was a sample of glucose made for confectioners' use. If we exclude it we get the following general results:

1st. The percentage of reducing substance obtained is nearly 82.00.

2d. The average reading of the cane sugar scale is nearly 25.5 divisions.

3d. If the pure glucose present is mono-rotatory, the specific rotatory power θ would be $\theta = \frac{8°.85 \times 100}{2 \times 8.2} = 54$ nearly. $80°.85$ is the angular rotation (half shadow) corresponding to 25.5 divisions of the scale, but the specific rotatory power of pure glucose for the half shadow polariscope is nearly 50. We have then here an excess of θ equal to 4.

4th. This excess is due to the presence of optically active matter of a higher specific rotatory power than pure glucose, which has not been changed even by prolonged boiling with dilute acid. I conclude, therefore, that it is quite difficult to convert the whole of the optically active matter into pure mono-rotatory glucose.

EXAMINATION OF MIXTURES.

In the examination of mixtures of cane sugar and grape sugar, it is necessary first to obtain the direct reading. Afterwards the cane sugar is to be inverted, using at most not more than ten minutes for this, and keeping the temperature at 68°. It is simply necessary to heat to 68° and then quickly cool.

After inversion the temperature is carefully noted and another reading taken. Then by Clerget's table the percentage of cane sugar is calculated. This, however, will only be approximately correct.

We next calculate the whole amount of rotation produced by the approximate amount of grape sugar present. Having determined this, the reading after inversion is to be corrected for the effect of inversion on the rotatory power of the grape sugar present. The average correction, when the heating has been carried just to 68°, will be about 2 per cent. of the whole rotation due to the grape sugar. If the process of inversion is carried on for an hour, as is the practice of some, the correction may amount to 10 per cent.

If the amount of glucose present is very small, this correction can be neglected. But if the amount is large, a failure to correct will introduce an appreciable error into the result. If animal charcoal has been used, a correction must be made also for it, depending, as has been shown, upon the amount employed, and also upon some other conditions which are not yet clearly made out.

It is easy to see into how grave an error we might fall, should we attempt to intimate directly the percentage of reducing substance present in such mixtures, from its rotatory power. I have shown in a previous paper that the percentage of such reducing substance is not *directly* but *inversely* as its rotatory power.

The error would be equally as grave if the amount of the grape sugar present should be computed by using a factor supposed to represent the amount of such substance for each division of the scale. Such a method is based upon the assumption that the rotatory power of grape sugar is constant and proportional to the reducing substance present. My paper already mentioned shows that this assumption is false.

SYRUPS.

When we come to the syrups of commerce, the case becomes still more difficult. These syrups are glucose adulterated with so-called cane syrups, *i. e.*, with the drippings and refuse of the sugar refineries. Among the syrups which are commonly used I may mention the "Revere" and the "Continental."

A "Revere" syrup which I examined had a specific gravity of 1.425, and contained 34.5 per cent. cane sugar.

A "Continental" syrup had a sp. gr. of 1.415 and 35.7 per cent. cane sugar. It also contained of inverted sugar 32.64 per cent.

It is easy to see how the admixture of such syrups with glucose tend to demoralize the results of the alkaline copper test and mystify the readings of the polariscope.

No wonder that heretofore such egregious blunders have been committed in these examinations. It is only when they are made with a full knowledge of the optical peculiarities of the commercial glucose itself, and of the composition of the cane syrup employed, while at the same time attention is paid to the changes produced by inversion and classification, that they can be relied upon as correct.

OBSERVATION TUBES.

In the polariscopic observation of inverted sugars, I use a copper tube silver plated inside and out. I find the most convenient length to be 110 m.m.

This enables the readings to be made without the trouble of neutralizing the acid.

The silver plating of the tube is not necessary, but it makes the working with it a little cleaner. Pure copper can be used without any danger whatever of the acid acting on it.

I use a tube of thin copper and of small diameter. Such a tube, when filled, quickly takes the temperature of the surrounding air. A few c.c. will fill one of these tubes. I have found by experiment, that when such a tube is filled with a liquid several degrees above or below the temperature of the air, in twenty minutes it will differ by less than half a degree from the temperature.

If an ordinary glass tube is employed, it is quite difficult to say how much time will be required to restore the equilibrium of temperature. My experiments show that it will require from two to three times as long.

I also provide this tube with a metallic jacket very conveniently made of a piece of zinc tubing. This jacket is a little less in diameter than the metallic caps of the tube, and is of such a length that when the caps are screwed on, the jacket fits against a shoulder turned on them.

The joint is made water-tight by using a rubber packing. This jacket is furnished with three open rings, fitted with short tubes. That in the center carries a thermometer, and those at each end serve as supply or exit tubes for any liquid which we may wish to pass through the jacket. By simply drilling a hole in the trough of the polariscope for the exit tube, the whole apparatus can be placed at once in position.

If now you wish to make a reading at a temperature say of 88°, it is done in the following way. A large flask or tank placed at one side and above the polariscope, and holding several liters of water, is heated to a temperature of about 92°. By a rubber tube, this is

connected, on the principle of a syphon, with the observation tube and its jacket. By means of a pinch cock attached to the exit tube, the hot water is allowed to flow through the jacket until the thermometer shows the temperature desired. It is hardly necessary to say that the observation tube must be filled at a temperature near that at which the reading is to be made, to prevent expansion. If we desire to make a reading at 0°, corresponding to 44° to the left, Clerget, we replace the water by alcohol which is cooled by a salt and ice bath to —3° or —4°.

The apparatus is then used as before. We have thus a means of making readings at any desired temperature without having to mutilate the polariscope, as is done by fitting it with a water bath. I will say, however, that a judicious use of Clerget's principle renders readings at a given temperature unnecessary. They are, however, useful in certain complex mixtures by doing away with certain calculations.

I propose next to extend my investigations to candies and other confections in which glucose enters as an ingredient.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office,** by ARNO BEHR.

Oct. 5, 1880.

232,889.—*Apparatus for extracting metal from ores.* THURSTON G. HALL.

232,922.—*Manufacture of Soap.* LOUIS BASTET.

A compound of soap and mineral oil, with or without the addition of boracic acid.

232,974.—*Vulcanized plastic compound.* ALFRED B. and CHARLES JENKINS.

Use infusorial earth as an admixture to ordinary vulcanized india-rubber.

232,991.—*Method and Apparatus for obtaining ammonia.* HANS P. LORENZEN.

See German Patent, p. 302.

232,995.—*Process and apparatus for preparing saccharate of lime and obtaining sugar.* HENRY A. J. MANOURY.

This process has been sufficiently described in the current literature. It is patented in France and Germany since 1877, and extensively adopted in Europe for the recovery of sugar from beet-root molasses.

Oct. 12, 1880.

233,070.—*Manufacture of wood pulp for paper.* JEFFERSON CHASE.

It is produced by reduction between revolving stones of brush, twigs, and small branches of trees, in their natural state.

233,144.—*Coating rubber with metal.* JOHN A. DALY.

For dentistry.

233,197.—*Lubricating composition.* CHARLES F. BROADBENT.

A mixture of milk of lime, precipitated chalk, and a solution of carbonate of soda, to be mixed with any ordinary lubricating oil.

233,217.—*Process for preserving fruits and other articles.* MARION F. DERBY.

The preserving agent is sulphurous acid gas, partly free and partly absorbed in an alum solution, to be poured over the articles.

233,296.—*Enameled rubber-cloth.* EDGAR M. STEVENS.

Oct. 19, 1880.

233,332.—*Method of and apparatus for bottling and barreling malt and fermented liquids, under pressure.* JOHN C. DE LA VERGNE and JULIUS J. SUCKERT.

233,453.—*Process of purifying fats and oils.* ALEXANDER W. WINTER.

The liquid or liquified fat is mixed with a certain proportion of Fuller's earth.

233,458-460.—Three patents relating to the *manufacture of artificial indigo*, taken by ADOLF BAEYER, in Munich.

The first Patent claims the production of orthonitrodibromhydrocinnamic acid, from orthonitrocinnamic acid and bromine ; the third, the production of orthonitrophenylpropiolic acid, prepared from the first named compound, by boiling with alcoholic potash ; the second, the production of orthonitrophenyloxacrylic acid from orthonitrocinnamic acid and hypobromous acid, and subsequent treatment with alcoholic potash. Concerning the relations of these products to indigo, see Patent 227,470, p. 228.

233,465.—*Red coloring matter.* HEINRICH BAUM.

This is the product of the reaction of diazoazobenzole with beta-naphtholedisulpho acid.

233,497.—*Lubricant.* SAMUEL FRAZER.

A compound of sal-soda, water, lime, and four qualities of rosin-oil, described in the specification.

233,502.—*Compound for pavements, drain-pipes, etc.* J. PIERSON GRANT.

Coal-tar, asphaltum, sulphur, iron filings, rosin, linseed-oil and sand.

233,505.—*Apparatus for extracting metals from ores.* THURSTON G. HALL.

233,558.—*Process of treating pyroxyline in the manufacture of plastic compounds.* JULES and CHARLES SCHMERBER.

233,568.—*Process of and furnace for reducing oxides to the metallic state.* THOMAS SOUTHAN.

Refers to the reduction of iron ore, without the production of slag.

Oct. 26, 1880.

233,600.—*Process of reclaiming rubber from old and waste vulcanized rubber, and utilizing the same in manufacturing rubber goods.* JOHN H. CHEEVER.

The old vulcanized rubber is boiled in raw petroleum.

233,600.—*Galvanic Battery.* JOSEPH H. CHEEVER.

233,680.—*Manufacture of carbon bisulphide and sulphuric acid from pyrites, and apparatus therefor.* ELIE C. E. and LÉON L. LABOIS.

Part of the sulphur is extrated from pyrites by distillation, and serves for the manufacture of carbon bisulphide in the ordinary way; the rest is obtained by roasting, and used in the manufacture of sulphuric acid.

233,716.—*Compound for Soap.* JOHN F. TYRRELL.

233,728.—*Condensed cider compound.* EDWIN R. CLEVELAND.

Concentrated cider or apple juice with salicylic and aromatic sulphuric acids.

233,750.—*Desiccating eggs.* HALVOR HALVORSON.

233,799.—*Extracting gold and silver from ores.* JAMES V. POMEROY.

Introduces chlorine gas or chloride of lime with an acid, into the pulverized ore with the mercury in the amalgamating process.

233,860.—*Process and apparatus for generating gas.* ERAZM J. JERZMANOWSKI.

A fluxing material is added to the coal used for making water gas, which, uniting with the ash of the coal, produces a fluid slag. To prevent the latter from clogging, a bath of molten iron is kept in the base of the furnace.

233,861.—*Process of producing hydrogen.* ERAZM J. JERZMANOWSKI.

A mixture of water gas and superheated steam is passed over highly heated blocks made essentially of alkaline aluminates. Under these conditions the carbonic oxide is transformed into carbonic acid, which is afterwards eliminated by absorption.

233,862.—*Process of and apparatus for making illuminating gas.* ERAZM J. JERZMANOWSKI.

233,875.—*Mixed phosphatic manure.* JOHN C. PERKINS.

233,885.—*Art of preparing waste vegetable products for use and transportation.* WM. HARROLD SMITH.

Compresses the material in a heated state (150—500° F.) in moulds, and forms solid blocks of it, without any other admixture.

233,886.—*An article for cattle food.* WM. HARROLD SMITH.

Compressed bran.

233,887.—*Fuel.* WM. HARROLD SMITH.

Compressed saw-dust.

233,900.—*Producing aluminium bronze.* JAMES WEBSTER.

Copper electroplated with aluminium is melted altogether with an alloy of copper, nickel, aluminium and tin.

233,916.—*Manufacture of aluminous cake.* GEORGE F. BIHN and ROBERT HEERLEIN.

Sulphate of alumina containing iron is treated in a semi-fluid state with alkaline sulphites.

233,948.—*Manufacture of artificial marble or stone.* ALVIN M. RICHARDSON.

233,960.—*Artificial stone and marble.* WILLIAM H. YOUNG.

234,025.—*Apparatus for burning sulphur to produce sulphuric acid.* HENRY GLOVER.

Foreign Patents.

Condensed from R. BIEDERMANN'S Report to the German Chemical Society, by OTTO H. KRAUSE.

KARL MOELLER, Kupferhammer, near Brackwede: *Improvements in apparatus for filtering vapors and gases.* (Germ. P., No. 10451, Jan. 22, 1880, being additional Patent to Germ. P., No. 8806. See this JOURNAL, **2**, 191.)—The additions relate to arrangements for keeping the filters moist, for scraping off dust and soot, and for regulating the temperature.

T. H. COBLEY, Dunstable: *Method of working up manure straw.* (Engl. P., No. 3312, August 16, 1879.)—The manure is digested with calcium sulphide and boiled with water, to obtain ammonia. After separating the liquid, the straw is treated with alkali, and the cellulose which results is used in the manufacture of paper.

PAUL STUBE, Paris: *Manufacture of illuminating and heating gas.* (Engl. P., No. 3302, August 16, 1879.)—Water gas, prepared in a retort from heated coal and steam in the usual way, is carburetted in a second retort by means of oil, fat, rosin, tar, etc., in the usual way, and freed from carbonic acid by milk of lime in the usual way. The carbonic acid, however, is removed by means of an ammoniacal solution of copper, which can be regenerated by heating. Besides this, the patent contains Mallet's process for preparing oxygen from air, and Tessié du Motay's method of obtaining it also from air, by means of alternate treatment of heated sodium permanganate with air and superheated steam.

EMIL DREYSSIG, Ravensburg: *Tar varnish.* (Germ. P., No. 10685, Nov. 13, 1879.)—Tar heated to 70° C., with equal weight of hydraulic lime, Roman or Portland cement. This varnish is not acted upon by acids, and is adapted for coating wood exposed to water, etc.

JACOB ENGELS, Kalk: *Explosive made from pyroxyline, nitroglycerine, pyropaper, xyloidine, nitromannite and silicate of soda, which explodes at a low tempera-*

ture, with or without a percussion cap. (Germ. P., No. 10232, Nov. 28, 1879.)—The above substances are mixed in various proportions, and put up in the form of cartridges, which are covered with a collodion capsule.

GUSTAV MOYSAN, Champigneuelles: *Method of refining blast furnace slag* (Germ. P., No. 10149, May 30, 1879.)—Blast furnace slag which, owing to its chemical composition, is unfit for making slag bricks or stones, is run into a movable refining furnace, where it receives such additions as will render it suitable for that purpose.

PAUL MAGNIER and L. F. DOERFLINGER, Paris: *Improvements in the method of dissolving silk and applying it to properly prepared fabrics.* (Germ. P., No. 10416, Oct. 15, 1879, being additional Patent to Germ. P., No. 7275, Feb. 13, 1879.)—Oxalic acid or potassa, soda or ammonia, are used as solvents.

P. SCHUETZENBERGER and L. NAUDIN, Paris: *Bleaching of vegetable fibres.* (Engl. P., No. 3290, Aug. 14, 1879.)—Sodium hydrosulphide is added to the alkaline bath to which the fibres are subjected, previous to treatment with chloride of lime.

JUL. ATHENSTAEDT, Bad Essen: *Method of preparing aceto-lactate and aceto-citrate of alumina.* (Germ. P., No. 10488, Jan. 6, 1880, being additional Patent to Germ. P., No. 9790, Nov. 24, 1879. See this JOURNAL, **2**, 232.)—Solution of lactic or citric acid, or of lactate or citrate of alumina, is added to solution of acetate of alumina, and the mixture evaporated.

EDWARD PERGER, Vienna: *Method of obtaining the volatile products emitted from roasting coffee.* (Germ. P., No. 10519, Dec. 25, 1879.)—These products, which may amount to 25 per cent. of the weight of the coffee, are condensed and used in flavoring coffee surrogates.

ALEX. WILKINSON, London: *Method of isolating telegraph wires.* (Engl. P., No. 3472, Aug. 28, 1879.)—Composition of flour, linseed oil, guttapercha and white lead.

ALEX. MANBRÉ, London: *Treatment of starch residues.* (Engl. P., No. 3481, Aug. 29, 1879.)—The starch retained in the waters is converted into glucose by adding an acid and heating.

JOHN TAYLOR, Southport: *Manufacture of ink.* (Engl. P., No. 3499, Sept. 1, 1879.)—Aniline black.

J. TOWNSEND, Stassfurt: *Improvements in the manufacture of alkaline carbonates, chlorine and hydrochloric acid.* (Germ. P., No. 10641, Oct. 18, 1879.)—Magnesium sulphate and potassium or sodium chloride are heated together with silica or clay, and in the presence of air, in a muffle furnace, to 500–700° C. Chlorine is evolved, and potassium or sodium sulphate and magnesia remain. Kainite is subjected to a similar treatment in presence of air or steam.

G. BORSCHE and J. BRÜNJES, Leopoldshall: *Method of obtaining sodium magnesium chloride and potassium magnesium sulphate from kainite.* (Germ. P., No. 10701, Dec. 20, 1879.)—Kainite is treated at temperatures below 80° C., with a solution of the same mineral in water, saturated at the ordinary temperature. Upon cooling, potassium magnesium sulphate crystallizes, whilst sodium and magnesium chloride remain in solution. If water alone be used in extracting, the sulphate is largely contaminated with sodium chloride.

THE AMERICAN CHEMICAL SOCIETY.

XLII.—Proceedings.

Regular Meeting, Thursday, November 4th, 1880.

Dr. A. R. Leeds in the chair.

In absence of a quorum, regular business was deferred, and the following papers were read:

1. "Isomorphous Salts and Fractional Crystallization." By Lucius Pitkin.

2. "On the Production of Ozone, by Heating Substances containing Oxygen." By Dr. A. R. Leeds.

3. "On the Action of Hyponitric Anhydride upon Organic Bodies." (Second Paper.) By Dr. A. R. Leeds.

In discussing Mr. Pitkin's paper, Dr. Endemann stated that he was glad that the incidental remarks made by him on a previous occasion had led Mr. Pitkin to prove, beyond doubt, the existence of real chemical compounds.

After which Mr. Stebbins made some statements on "New Coloring Matters, produced by the Action of Nitrosodiumethylaniline hydrochlorate on Sulphuretted Phenols."

After which Mr. Casamajor made a communication "On a Process for Detecting Starch Sugar, mixed with Commercial Cane Sugar."

The report of Committee on the Nomination of Officers was then read by Mr. Casamajor. The names of the President and Vice-Presidents were left out, as is the usual custom, and the other officers nominated are as follows:

Corresponding Secretary:

P. Casamajor.

Recording Secretary:

Albert H. Gallatin.

Treasurer:

W. H. Nichols.

Curators:

Wm. Rupp, A. J. Rossi, A. A. Fesquet.

Committee on Papers and Publications:

ARNO BEHR, GIDEON E. MOORE, A. R. LEDOUX.

Committee on Nominations:

WILLAM GEYER, O. KRAUSE,
JAS. H. STEBBINS, ARTHUR H. ELLIOTT,
J. C. BATTERSHALL.

Board of Directors:

P. CASAMAJOR, C. F. CHANDLER,
ALBERT H. GALLATIN, H. MORTON,
W. H. NICHOLS, W. M. HABIRSHAW,
E. WALLER, M. ALSBERG,
A. R. LEDOUX. J. GOLDMARK.

Mr. STEBBINS announced a paper for the next meeting "On some New Azo-Colors."

A vote of thanks to Mr. FESQUET for the microscope presented to the Society, was carried unanimously.

After which the meeting adjourned.

ARTHUR H. ELLIOTT,
Recording Secretary.

XLIII.—ISOMORPHOUS SALTS AND FRACTIONAL CRYSTALLIZATION.

BY L. PITKIN.

In discussing a paper of mine read before this Society at the May meeting, Dr. Endemann suggested that the substances described by me might not be definite chemical compounds, but mixtures of isomorphous salts. This explanation, while accounting for both bromine and chlorine in the same salt, and under some circumstances a plausible one, can not to my mind explain the phenomena described.

Two facts, neither of which can, I think, be disputed, stand out prominently in considering the subject of isomorphism. The first is, that the resulting mixed crystal has a composition dependent on the ratio, one to the other, of the isomorphous salts in solution, or the constituents forming these salts.

The second fact may be formulated as follows: When two isomorphous salts, together in solution, are subjected to fractional

crystallization, the salts differing in their degree of solubility in the menstruum employed, the crystals first formed will contain relatively a greater amount of the more insoluble salt, while the crystals formed at the end will be correspondingly rich in the more soluble salt.

Judged by these rules, Dr. Endemann's supposition seems to be contradicted by the facts brought out in the investigation.

In regard to the rule first laid down, I would call the attention of the Society to the dibromated compound, $K_2PtBr_2Cl_4$, described at the November meeting; this was formed when 0.5 grm $PtCl_4$ was added to 4.0 grms KBr in solution, the solution being kept cold. It will be perceived that the amount of KBr is here 12 times the quantity required to form the compound in question, yet in 3 experiments, the amount of Pt yielded on decomposing the salt, was 34.32 against a theoretical 34.35 per cent.

Not only this, but the experiment was performed under varying circumstances since, preserving the same amount of platinic chloride and potassium bromide in all, to the solution from which the first crystals were obtained, were added 2 c.c. of concentrated HCl, to the second solution 1 c c., and the third solution none at all.

It would be supposed, that under these circumstances, the compound formed in the solution strongly acid, with HCl, if really a mixture of isomorphous salts, would contain more of the double chloride; but an analysis of the three salts produced showed no such result.

It is, however, chiefly on the second rule, that of fractional crystallization, that I would depend, as proving the chemical as opposed to the mechanical nature of these compounds.

The rule involved in fractional crystallization presupposes a difference in the solubility of the salts to be separated. If these salts are not isomorphous, they can be separated completely; on the other hand, if they have the same crystalline form, the crystals will contain both salts, one in part substituting the other.

Now, if the solution of these isomorphous salts of different solubility, is fractioned, the crystals produced will contain different proportions of the two salts, if they are mechanical compounds, while if a definite compound salt has been formed, the crystals produced at different concentrations will have a constant composition.

As to the constancy of these salts under fractional crystallization, let me select, as an example, the monobromated compound. In order to form it, 4.888 grms of K_2PtCl_6, and 1.512 grm of K_2PtBr_6, were employed. Three crops of the crystals yielded respectively, 36.97,

37.04 and 36.99 per cent. of platinum; the theoretical percentage being 37.05.

It now remains to consider the difference in solubility of the double bromide, and double chloride of platinum and potassium.

As these salts were crystallized from boiling solutions, a comparison of solubility in water at 100 ° C. will answer the question.

The solubility of the double chloride in boiling water, as given by Elliot and Storer, is 1 part of the salt in 19 parts of water.

The solubility of the double bromide has never, so far as I can find, been published in anything but general terms; Elliot and Storer stating, "sparingly soluble in water, insoluble in alcohol."

I found it necessary, therefore, to determine the solubility of this salt in boiling water.

10 grms of the double bromide were kept at the boiling point, with 50 c.c. H_2O, for four hours, the flask being frequently shaken. The flask was heated by being placed inside of a beaker of water, kept boiling; by this means, the contents of the flask were kept at 100° and, at the same time, so quiet, that a measured quantity of the clear solution could be easily removed by a pipette.

5 cubic centimeters were taken for the first trial, and yielded, by evaporation, and drying at 100°, 0.495 grm of K_2PtBr_6; after boiling one hour more, another 5 c.c. were taken, and 0.498 of the dried double bromide recovered; as 5 c.c. of water at the boiling point, weigh not quite 5 grms, the solubility of the double bromide in boiling water is, as near as possible, 1 part in 10.

In concluding, I would remark that in the case of the monobromated compound, it seems impossible, on the supposition of isomorphous mixture, to have the double bromide crystallize out each time in the right proportion, when but one-third as much of it was employed as of the double chloride, and when its solubility is twice as great.

School of Mines, Col. Coll., June 15, 1880.

XLIV.—On the Production of Ozone by Heating Substances Containing Oxygen.

By Albert R. Leeds, Ph.D.

In his excellent "Historisch-Kritische Studien über das Ozon," published December, 1879, Prof. C. Engler enumerates among the modes of formation of ozone, that of heating substances containing oxygen. This statement is founded upon the experiments published by Schönbein, as far back as 1855*, and which, although rendered of doubtful probability by the fact established by Andrews, that the decomposition of ozone into ordinary oxygen occurs at (and below) 270°, have never been formally refuted.

Schönbein was led to anticipate the results of his experiments by certain peculiar views concerning the state in which the oxygen existed in the bodies experimented upon. He thought that they contained the oxygen either partly or altogether in an ozonized condition, and he included in the number of such bodies the oxides and superoxides of all the noble metals, the superoxides and some acids of the common metals, and a number of the states of oxidation of non-metallic elements, *e. g.*, the peroxide of hydrogen, the various acids of nitrogen, of chlorine, bromine, and iodine, or in general, *all those substances which evolve oxygen on heating.* Furthermore, the reason, according to Schönbein, why these bodies underwent decomposition under the influence of heat, was that the ozone which they contained was partly resolved into ordinary oxygen on heating.

In the conduct of his experiments, Schönbein thought that he amply provided against the presence of oxides of nitrogen in the gas liberated on heating, by due care in the preparation of the bodies experimented upon. The peroxide of lead, for example, he prepared from minium by means of acetic acid, the mercuric oxide from mercuric chloride, the argentic oxide from the sulphate, and so on. And while he recognized that the chlorates, bromates and iodates would evolve traces of chlorine, bromine and iodine, he ascribed to these substances only a part of the effect produced, assuming that the rest was due to ozone set free, on heating, at the same time. The apparatus employed was of the simplest description, merely in fact a test tube 6 in. in length and $\frac{1}{2}$ in. in breadth, in which the body was heated, and strips of moistened potassium-iodide-starch paper, or

* *Verhandl. d. naturf. Gesell.*, Basel, **1**, 252 ; *Journ. f. Prakt. Chem.*, **66**, 286 ; *Phil. Trans.*, 1860, 113.

paper dipped in freshly prepared guaiacum tincture held in the upper end of the tube.

Tried in this manner, all the substances experimented upon by Schönbein which gave off oxygen, gave at the same time the ozone reaction; the oxides of the noble metals, like argentic oxide, giving the reaction in the most striking manner, the peroxide of manganese very feebly.

In conclusion, Schönbein remarks that the escape of a portion of the liberated oxygen from the deozonizing action of heat, is a striking fact, beyond his power to explain.

Apparently unaware of the extended research of Schönbein, and of the theoretical grounds upon which that research was founded, Mr. Kingzett published in 1872, a preliminary note upon ozone*, in which he obtained results similar to those detailed above. After stating that the gas, evolved on heating mercuric oxide, even after its passage through a considerable depth of potash solution, turned potassium-iodide-starch papers blue, and that the same effect was produced by the gas liberated from native or artificial manganic dioxide, even when the dioxide was heated to redness, Mr. Kingzett states that "in short, from every source I have tried, the oxygen produced never lacked these properties."

In his critical history of ozone, Prof. Engler imputes to Mr. Kingzett the statement that the gas given off in these decompositions is ozone, but in justice to Mr. Kingzett it should be said that this is a slight misrepresentation, and that the latter states that he has no proof to offer that it is ozone.

In the same place, Prof. Engler states† that periodic acid on heating to 130–135° gives off ozonized oxygen, and quotes the experiments of Croft‡, that iodic acid, in the act of crystallization, gives off ozone. Also the statement of Bellucci §, that during the concentration of the aqueous solution of iodic acid, and also during the crystallization of the syrup obtained by concentrating, ozone is given off.

I have elsewhere shown that the apparent evolution of ozone from iodic acid, in process of concentration and crystallization, ceases when the iodic acid has been recrystallized a sufficient number of times to obtain it free from those traces of chlorine or nitrous acid,

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* *Chem. News*, **25**, 242.

† Historisch-Kritische Studien über das Ozon, p. 26.

‡ *Chem. News*, **25**, 87.

§ *Ber. d. deutsch. chem. Gesell.*, 1875, **8**, 905.

or possibly some lower oxide of iodine formed in the process of manufacture, and gradually eliminated by successive recrystallizations of the acid.

In the conduct of the experiments detailed below, two considerations were kept very prominently in view: 1st. To obtain the material experimented upon in as nearly as possible a state of purity. 2d. To absorb any gases, other than ozone, by washing.

To this end mercuric oxide was prepared by precipitation from the chloride by caustic potash, and washing by decantation and filtration, until no traces of either potash or hydrochloric acid could be detected in the filtrate. The oxide, weighing 54 grms after complete drying, was introduced into a piece of hard glass tubing, sealed at one end, and so cautiously heated in a combustion furnace, that the liberated gas came over at the lowest temperature of evolution and very slowly. The oxygen was passed first through a flask containing strips of filter paper, moistened with a two per cent. solution of fresh, unaltered resin of guaiacum in alcohol. These were gradually turned of a deep blue. The flask was then disconnected directly from the combustion tube, and a series of three Geissler absorption bulbs, each containing a very small amount of water (15 c.c.), was inserted between. After allowing the oxygen to bubble through the bulbs for six hours, fresh strips of moistened guaiacum paper placed in the flask were entirely unchanged. Upon the addition of silver nitrate to the wash waters, they gave an unmistakable reaction for chlorine.

It follows, therefore, that it is practically impossible to wash out from the mercuric oxide prepared as above, every trace of chloride, and that sufficient remains to give on heating a reaction for chlorine, or as Schönbein thought, for ozone.

Manganese dioxide was prepared by digesting the sulphate with chloride of lime. After the decomposition was complete, the precipitate was washed *more than thirty times*, until finally no trace of chlorine could be detected in the wash water. The dried peroxide was then heated in the combustion furnace to such a temperature, that a slow evolution of oxygen took place during eight hours. No change of the moistened guaiacum papers occurred in contact with the evolved oxygen, either before or after its passage through the Geissler bulbs, neither could any reaction for chlorine be obtained with the wash water. It may be stated, accordingly, that artificial manganic peroxide prepared with due care, gives on heating no reaction for ozone, or for any gas which could be mistaken for ozone.

Native manganic peroxide, on the contrary, heated for six hours in like manner, affected the guaiacum test when placed before the wash bottles, but not when it was put after. In the latter case, the wash water itself gave the reaction for chlorine.

Plumbic peroxide was prepared from the acetate by digesting with chloride of lime, and washing between thirty and forty times, or until the filtrate gave no reaction for hydrochloric acid. On cautious heating for six hours, the evolved gas affected the guaiacum when placed before the wash water, but not when it was put after; the wash water, in the latter case, giving the chlorine reaction.

Some argentic oxide was prepared from pure silver, obtained by reduction from the chloride. After conversion of the silver into sulphate, the oxide was thrown down by potash, and washed with boiling water, until no traces of chlorine, etc., could be detected in the filtrate. The argentic oxide was then transferred to a small retort, which was heated by an oil bath. Air, passed previously through a train of purifiers, was drawn through the retort in a slow stream during the heating. After leaving the retort, it pased over a strip of moistened guaiacum paper, then through three Geissler bulbs, containing water, and finally through a flask containing another strip of guaiacum paper. In the first experiment, the first guaiacum paper became strongly colored when the temperature of the oil bath was raised to 190°, the second when the temperature had reached 213°.

This result made it appear probable that the air of the laboratory was not sufficiently purified, and the experiment was again repeated with outside air. Identical results were obtained, the first paper changing at 190°, the latter at somewhat higher temperature, and the heating being continued until the oil bath had risen to 280°. An experiment was then made in blank, purified air being drawn through the train of apparatus without heating the argentic oxide, when it was found that both papers altered in contact with the air alone, though at a slower rate than in the previous experiments, when the air was heated.

Having established in this manner, that the change of color of the guaiacum tests was insufficient to prove the presence of ozone, they were replaced by zinc-iodide-starch papers. On raising the temperature of the retort containing the argentic oxide to 284°, the first iodide paper turned blue, the second, which was placed after the series of Geissler bulbs, remained entirely unaffected. The reaction was due to the presence of a trace of chlorine, but some difficulty was experienced in demonstrating this to be the fact. The

wash water gave so faint an indication, that it was not until the whole amount of wash water in the three bulbs, amounting in all to 45 c.c., had been evaporated down to 5 c.c., that an unequivocal reaction for chlorine was obtained.

Some periodic acid was then prepared by digesting 1 pt. of iodine with 20 pts. of sodium carbonate in 200 pts. of water, and passing a stream of chlorine through the liquid until no further precipitate was formed. The sodium periodate was then filtered, slightly washed with cold water, dissolved in dilute nitric acid, and decomposed with argentic nitrate. The resulting diargentic periodate was crystallized out of its solution in hot nitric acid, decomposed with cold water, and the aqueous solution of periodic acid thus formed evaporated to dryness six or seven times, until no trace of acid fumes could be detected in the escaping moisture. The periodic acid was heated in a retort placed in an oil bath, a slow stream of purified air being drawn over it during the course of the operation, and at no time was the temperature allowed to rise above 154°. In the first set of trials, the guaiacum papers placed before and after the Geissler bulbs containing the water employed in washing the gas, were colored blue. After the discovery that the air alone could effect this change, zinc-iodide-starch papers were employed, when the paper placed before the wash waters was turned blue, that placed after remained unaltered. The wash waters gave an unmistakable reaction for chlorine.

The conclusion to be drawn from the foregoing experiments is, that the supposed evolution of ozone upon heating certain oxides of both metallic and non-metallic bodies, is in reality due to minute traces of impurities, usually chlorine, which cannot be eliminated in the ordinary course of preparation of these bodies.

XLV.—On the Action of Hyponitric Anhydride on Organic Bodies.

By Albert R. Leeds, Ph.D.

[Second Paper.]

In a preceding paper (Journal American Chemical Society, **2**, 277) I have given the results which were obtained when hyponitric anhydride was made to act at various temperatures upon benzene, naphthalene and cymene. My object in the present paper is to present, in conformity with the promise made at that time, the results of the action of hyponitric anhydride upon a variety of other organic bodies.

IV.—ACTION UPON TOLUENE.

In the latter part of May, 250 grms of toluene were treated with the anhydride until the product ceased to increase in weight. It was then poured from the five flat evaporating dishes, in which it had been hyponitrified, into a flask, and left with only a sheet of filter paper tied over the mouth of the flask, until the end of the following September. By this time all smell of the excess of dissolved anhydride had diffused off, and a red oil remained, with numerous large white crystals at the sides and bottom of the flask. These were filtered off together with some adherent yellow solid matter, and on examination proved to be oxalic acid. To get rid of the oxalic acid the entire mass was dissolved in hot water, from which a large crop of crystals separated on cooling, the oxalic acid, together with a yellow coloring matter, going into solution. The crystals thus obtained were repeatedly crystallized out of boiling water, until they became almost colorless. Afterwards, being small and not well defined, they were crystallized out of alcohol, benzene and chloroform, but not with much greater success. The latter solvent afforded them in nodular masses, composed of white translucent leaflets, which polarized under the microscope. Considerably below 200° the crystals begin to sublime, and are slowly volatilized without melting or undergoing decomposition, even when the temperature is raised as high as 230°. The product, purified as far as possible by repeated crystallization from boiling water, was accordingly transferred to a retort and kept in the air bath at the temperature of 170°, until all the crystalline substance was sublimed over. The crystals thus obtained were readily soluble in hot water, alcohol, benzene and chloroform, but in cold water almost insoluble.

On analysis they were found to contain:

	I.	II.
Carbon	52.33	53.23
Hydrogen	3.75	5.08

These figures closely approximate to the composition of dioxybenzoic acid, $C_6H_3(OH)_2.COOH$, the discrepancy being in a somewhat low percentage of carbon. In order to ascertain whether a different result could be obtained by further purification of the substance, it was once more sublimed, this time at a temperature of 220°, twice dissolved in boiling water, allowed to cool after each solution, filtered, washed and dried over sulphuric acid.

0.1979 grm of the substance yielded on combustion, 0.3888 grm carbonic acid, and 0.0691 grm water, corresponding to

	Found.	Theory.
Carbon	53.58	54.54
Hydrogen	3.88	3.89

This would add a fifth to the four previously known of the six possible modifications of dioxybenzoic acid. From three of these, protocatechuic acid, oxysalicylic acid and the dioxybenzoic acid (1:2:4), it differs both in its melting point and in not yielding a coloration with ferric chloride.

It agrees most nearly with the modification, which has been obtained by Barth and Senhofer*. By heating benzoic acid along with sulphuric acid and phosphoric anhydride to 250°, in sealed tubes, they produced a disulphobenzoic acid, the potassium salt of which, when melted with potash, yielded the modification of dioxybenzoic acid referred to. But the new modification differs from this body by its not forming a hydrate when crystallized out of hot water. It is anhydrous, whilst the acid of Barth and Senhofer in the air-dried state, contains $1\frac{1}{2}$ molecules of water. Unlike this acid, which melts with decomposition at 222°, it does not melt, but begins to sublime at 170°, and may be sublimed without undergoing change, even when the temperature is raised as high as 230°. The acid of Barth and Senhofer, when heated with strong sulphuric acid, dissolves to a red liquid that deposits a green powder on the addition of water. In the case of the new acid, its solution in sulphuric acid is not colored. It forms readily soluble salts with the alkalies, alkaline earths and with lead. Its silver salt, which while somewhat soluble in water, is the least soluble of the salts thus far made, crystallizes in thin transpar-

* *Ann. Chem. Pharm*, **159**, 217; **164**, 109.

ent plates with a silky lustre. Unlike the silver salt of the acid obtained by Barth and Senhofer, which contains 1 molecule of water of crystallization, this salt is anhydrous. Finally, the acid of Barth and Senhofer is described as crystallizing in prisms or thin needles, whilst the new acid, whether crystallized by sublimation or from solution, forms aggregates of small leaflets. From a consideration of all of these characteristic differences, it would appear that the new substance is one of the two remaining possible, but hitherto not isolated, modifications of dioxybenzoic acid.

The original oil, from which the oxalic and dioxybenzoic acids had been separated by filtration, on standing formed two layers, the lower of which a much lighter red color than the upper layer. These two portions were divided by a separating funnel, and distilled. The denser yielded mostly nitric acid, after which a small portion of oil came over, and lastly, a white crystalline sublimate. The lighter yielded first an oil and then a crystalline body ; both distillates apparently being identical with those obtained from the denser liquid. The amount of the crystalline product being small, it was feared that it could not be obtained in a pure condition from the large quantities of oil with which it was associated. All the distillates were therefore reunited and distilled with water. The oil came off plentifully along with the steam, at first of a light yellow color, and later on, as the distillation continued, of a yellowish-red to red color. On separating all the oil from the various portions of the distillate, and distilling it free from water, in a small retort, the temperature rose to 222° –223°, when it became constant, and most of the oil came off. Afterwards the thermometer rose to 228°–229°, when it again became constant, and the remainder of the oil came over, leaving only a very small residue, consisting of a dark reddish oil behind. Both portions had exactly the same beautiful tint of straw-yellow color. But the latter, with the considerably higher boiling point, was thought to be a different substance from the oil boiling at 222°, until its specific gravity was determined, which was 1.159. The specific gravity of orthonitrotoluene is stated to be 1.163, and both portions of the oil therefore were orthonitrotoluene.

As the oil was distilled off with the water in the original process of the purification, the residue became more and more solid, until finally, on cooling, the liquid became filled with crystals. These were purified by repeated crystallization from boiling water, in which they were readily soluble, until they were almost colorless. They were further purified by sublimation, the sublimed crystals

melting at 120°, which melting point, together with the white laminated appearance of the crystals formed by sublimation, and the characteristic odor given off on heating, proved the substance to be benzoic acid.

Finally there remained behind, after all the oil and benzoic acid had distilled over, a large amount of a very dark colored tarry residue. This was sublimed at a temperature of about 110°, yielding nearly 10 grms of beautiful light yellow crystals. These were needle-shaped, but clustered together so as to form feathery or arborescent crystals. Their solution in water was light yellow, staining silk permanently of the same color. No insoluble salt could be formed. After repeated sublimation, the melting point of the crystals was 109° to 110°, and since this is likewise the melting point of paradinitrocresol, $C_7H_6(NO_2)_2O$, the supposition first formed was that the new substance was no other than paradinitrocresol. The similarity in its dyeing and other properties, and its mode of derivation (paradinitrocresol being obtained by the action of nitrous acid on paratoluidine), gave to this supposition so strong a likelihood that it was abandoned only after repeated analyses. The first two analyses gave:

	I.	II.	Theory.
Carbon	39.26	39.60	42.42
Hydrogen	2.98	4.24	3.03
Nitrogen		14.19	14.14

A portion of the supposed paradinitrocresol, after resublimation, was crystallized out of its solution from alcohol. 0.2113 grm of this product gave 0.3016 grm carbonic acid and 0.0678 grm water, corresponding to

Carbon	38.92
Hydrogen	3.56

Two more analyses were made, with the result of showing that the new substance was not paradinitrocresol, $C_7H_6(NO_2)_2O$, but dinitro-orcine, $C_6H(CH_3)(NO_2)_2(OH)_2$, which differs from the former only in containing one more atom of oxygen. In other words, not only had two of the atoms of hydrogen in the toluene been replaced by NO_2, but it had been raised by oxidation to the condition of a derivative of orcine. Unexpected as was this result, yet it is fully confirmed, not only by these repeated analyses, but also by those made later upon the constitution of the salts. Comparison with dinitro-orcine, $C_6H(CH_3)(NO_2)_2(OH)_2$:—

	IV.	V.	Theory.
Carbon	39.99	38.55	39.25
Hydrogen.....	2.98	4.01	2.80
Nitrogen.....	13.82		13.09

Dinitro-orcine has already been obtained by Stenhouse and Groves*, by the action of dilute nitric acid in the cold upon nitroso-orcine; strong nitric acid forms trinitro-orcine. But the physical and chemical characters of the body obtained by Stenhouse and Groves, are altogether different from those of this new modification derived from toluene. In the absence of present knowledge as to the relative orientation of the NO_2 group in the two bodies, I shall designate the former as α, the latter as β-dinitro-orcine. The melting point of the former, as determined by Stenhouse and Groves is 164°.5, that of the latter is 109° to 110°. The former crystallizes in deep yellow rhomboidal plates; the latter as bright yellow needles, when prepared by sublimation, and as golden yellow needles, when crystallized out of alcohol. The former is almost insoluble in cold water, the latter is slightly soluble in cold, very soluble in boiling water. The alkaline salts of α-dinitro-orcine are very soluble in water, difficult to crystallize, and orange-red in color. The same is true of the solubility of the corresponding salts of β-dinitro-orcine, but their color is golden yellow. The calcium and lead salts of β-dinitro-orcine crystallize in yellow needles, the silver salt in plates. While barium forms with dinitro-orcine two hydrated salts, one of which is normal, the other acid, β-dinitro-orcine forms only one, and that the normal salt. It crystallizes in long reddish-yellow needles, which have the property not shared by any other of the salts so far examined, of exploding violently when heated. It crystallized likewise from alcohol, but not so well as from water, forming groups or nodules of small needles.

An attempt was made to form two salts with toluidine, by bringing one and two molecules of toluidine in alcoholic solution, into combination with one molecule of β-dinitro-orcine likewise dissolved in alcohol. The salts which were formed in both cases, after recrystallization from alcohol, had the same melting point of 108°. Whilst both crystallized in small yellowish-red needles, that with two molecules of toluidine was somewhat the lighter in color. For this reason, both salts were redissolved in water, in which they are readily soluble. They crystallized out in needles of the same color, but

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much larger than those obtained from the alcoholic solutions. The melting points of both substances still remained at 108°. An analysis of that prepared with a solution of two molecules of toluidine, and recrystallized from water, demonstrated that it contained in chemical combination but one molecule, and that both substances were the same body, the normal toluidine salt of dinitro-orcine or $C_7H_9N.C_7H_6(NO_2)_2O_2$.

0.1793 grm of the salt yielded 0.3566 grm of CO_2 and 0.0852 grm of water, corresponding to

	FOUND.	THEORY.
Carbon	54.24	54.72
Hydrogen	5.28	4.89
Nitrogen		9.12
Oxygen		31.27

The amide was prepared by reduction of the β-dinitro-orcine by means of tin and hydrochloric acid. After complete reduction had been effected, the tin was precipitated by sulphuretted hydrogen, the stannous sulphide filtered off, and the filtrate evaporated to dryness. The amide was left as a dark reddish-brown powder. Attempts made to obtain it in a crystalline form, by the use of various solvents and by sublimation, were unsuccessful.

In concluding this part of the subject, it should be mentioned that the aqueous solutions of β-dinitro-orcine and certain of its salts, dye silk a permanent and very beautiful yellow color. Its ready preparation by the treatment of toluene with hyponitric anhydride, and its relatively large yield therefrom, may render its practical application in the arts of some future importance.

XYLENE.

250 grms of xylene, after treatment with hyponitric anhydride in the same manner as the toluene, at the expiration of a like interval of 5 months, were found to have yielded an abundant crop of large colorless crystals along with some adherent solid matter, and a supernatant yellowish-red oil. No unaltered xylene remained. The solid portion, by treatment with successive portions of water, was separated into oxalic acid, which had constituted the colorless crystals alluded to above, and another white crystalline body with a melting point, as determined after repeated crystallizations, of 192°–193°. A combustion performed on 0.1537 grm of this latter substance yielded 0.3255 grm CO_2 and 0.0566 grm H_2O, from which it appears that its formula is identical with that of phthalic acid, $C_6H_4(COOH)_2$:—

	FOUND.	THEORY.
Carbon	57.75	57.53
Hydrogen	4.09	3.62
Oxygen		38.85

The oily portion was distilled with water, and the oil which came over in the distillate was purified by repeated distillation in a current of steam, until its boiling point became constant. This was at 234°, proving that the light yellowish-red oil thus obtained, was ortho-nitroxylene. On cooling, the water in the retort deposited crystals, which after being repeatedly recrystallized from boiling water, proved to be paratoluic acid. The insignificant amount of reddish solid residue finally left in the retort, was found to consist merely of paratoluic acid with a small amount of oil.

PHENOL.

The phenol was attacked by hyponitric anhydride with great energy and rapidly converted into a blackish mass. On boiling this with water, and filtering from the carbonized residue, the solution deposited crystals which, on recrystallization, proved to be picric acid. This was the only substance present; instead of obtaining, as in the case of the substances previously experimented upon, a mixture of nitrified and oxidized bodies.

ANILINE.

Aniline was likewise very energetically attacked by N_2O_4, and converted into a black semi-solid mass. When this was treated with hydrochloric acid a portion dissolved in the acid, and was again precipitated by potash. On attempting to sublime the original nitrated product, a large amount of aniline was distilled off, but no crystalline sublimate was obtained. Another portion was prepared, and a portion subjected to very careful distillation, the temperature of the retort being kept at about 185°. A light red oil was given off at this temperature, which gradually became darker in color. After several hours the entire mass was carbonized, but no crystalline sublimate came over. Another portion of the raw product was boiled with water and filtered while hot, and then, becoming turbid on cooling, was again filtered. It yielded a dark red liquid. This was evaporated to dryness, on the water bath, leaving a blackish solid residue. This residue was then redissolved in water, and again evaporated to dryness when it had lost most of its tarry properties, though it did not present a crystalline appearance. On heating, it

gave off only a few drops of oil until, the temperature having been raised very slow y to 174°, it gave a violent puff and carbonized.

Having failed to obtain from aniline any results by methods similar to those which had proved successful with the other substances experimented upon, various portions of the aqueous residue were dissolved in alcohol, ether, chloroform, hydrochloric and acetic acids. The chloroform appeared to answer best because it dissolved the smallest amount of the tarry matter, and from the solution some needles crystallized out. But they were in quantity too small to admit of their analysis, nor was a more successful result obtained when the entire aqueous residue from another portion of the nitrated aniline was treated in like manner. What, however, we had failed to do with care was apparently accomplished in one instance by accident. A portion of aniline, amounting to about 100 grms, was treated with hyponitric anhydride for a shorter period than usual, a considerable amount of the aniline being left unacted upon. On expelling the excess of aniline by boiling with water, a crop of crystals separated out at once from the cold aqueous solution. These crystals were repeatedly crystallized out of alcohol, until their melting point became constant at 123°. They were in the form of long needles, with a beautiful dark red color, and contained nitrogen; unfortunately only 0.0707 grm remaining after purification, for analysis. It gave 0.1883 grm CO_2 and 0.05 grm H_2O, corresponding to 72.63 per cent. of carbon, and 7.85 per cent. of hydrogen. Such a percentage of carbon could not be brought into harmony with any formula, and it was evident that the analysis was at fault.

It is useless to narrate the remaining unsuccessful experiments. On the supposition that a too long exposure to the hyponitric anhydride had, in all trials except the previous partly successful one, decomposed the nitro-derivatives first formed, various new portions of the aniline were treated with hyponitric anhydride for different periods, and the resulting products examined, but without success. My object in giving these details, at such length, is to assist any one who may in the future repeat these experiments. The properties and melting point of the body found differ widely from those of any of the nitranilines hitherto obtained, and there is little question of its being a new substance.

ORTHOTOLUIDINE, XYLIDINE, CRESOL.

The results arrived at with these bodies were still less satisfactory than those obtained with aniline. 100 grms of orthotoluidine (m. pt.,

199°) were treated with hyponitric anhydride for three hours, when the operation was discontinued, the toluidine apparently being completely changed and converted into a black solid. This product was boiled with water, the solutions after cooling filtered and evaporated to dryness. A purplish-black residue remained with some minute leaf-like crystals. This was transferred to a retort, and the temperature raised very cautiously. No sublimate came off below 135°, and at this point the substance was decomposed with a puff, leaving only some carbonized matter behind. On attempting to dissolve out, by the use of solvents, any crystalline bodies present in the residues obtained from the solution of other portions of orthotoluidine similarly nitrated, or to carry them over by distillation in a current of superheated steam, no results were obtained.

100 grms of xylidine, after nitration for four hours, and 100 grms of cresol, after nitration for twelve hours, were converted into blackish-red masses, which were treated in like manner with boiling water, and their aqueous solutions after filtration evaporated to dryness. Dark red residues were obtained from both substances, and these residues were decomposed at low temperatures when attempts were made to sublime them. Nor were any products obtained by the use of solvents, or by distillation in a current of steam.

ANTHRACENE.

Anthracene is converted by the action of hyponitric anhydride into anthraquinone. Along with the anthraquinone a small amount of red oil is formed, which is best removed by mechanical separation with filter paper, and by washing with ether. Since, in every other instance, besides a product of oxidation, some nitro or hydroxyl-derivative had been obtained, it was thought that a different result might be arrived at by operating upon a solution of anthracene in glacial acetic acid. 50 grms of anthracene, dissolved in 400 c.c. of the acid, yielded, after saturation with N_2O_4, 58 grms of anthraquinone. The theoretical amount of anthraquinone was 58.3 grms. A little red oil was formed at the same time, but no hydroxylated or nitro-derivative.

TABLE OF PRODUCTS OBTAINED BY THE ACTION OF HYPONITRIC ANHYDRIDE UPON ORGANIC BODIES.

		Oxides.	Nitro-derivatives.	Nitro-hydroxyl.	Hydroxyl-derivatives.
Benzene	C_6H_6	CO_2 $C_2H_2O_4.2H_2O$ C_6H_4O(M.P.215°)	$C_6H_5(NO_2)$	$C_6H_2(NO_2)_3OH$	$(C_6H_5.OH)$
Toluene	$C_6H_5.CH_3$	$C_2H_2O_4.2H_2O$	o—$C_7H_7(NO_2)$ (B.Pt., 222°)	β—$C_6H(CH_3)(NO_2)_2(OH)_2$ (M.Pt., 109°–110°)	$C_6H_3(CH_3)(OH)_2$ $C_6H_5.COOH$ $C_6H_3(OH)_2.COOH$
Xylene	$C_6H_4(CH_3)_2$	$C_6H_2O_4.2H_2O$	o—$C_8H_9(NO_2)$ (B.Pt., 234°)	?	$C_6H_4(CH_3).COOH$ $C_6H_4(COOH)_2$
Cymene.....	$C_6H_4.CH_3.C_3H_7$	$(C_2H_2O_4.2H_2O)$	α—$C_{10}H_{10}(NO_2)$	?	$C_6H_4(CH_3).COOH$
Naphthalene...	$C_{10}H_8$	$C_2H_2O_4.2H_2O$ $C_{10}H_4O_4$	$C_{10}H_7(NO_2)$ α—$C_{10}H_6(NO_2)_2$ β—$C_{10}H_6(NO_2)_2$	? ? ?	$[C_6H_4(COOH)_2]$ $C_{10}H_4(OH)_4$?
Anthracene....	$C_{14}H_{10}$	$C_{14}H_8O_2$			
Phenol..	$C_6H_5.OH$			$C_6H_2(NO_2)_3OH$	

CONCLUSION.

By an examination of the accompanying table of products, it will be seen that in every case except in those of anthracene and phenol, oxalic acid was one of the substances formed. That this should have happened with anthracene was not to be expected, inasmuch as anthracene is converted by direct oxidation into anthraquinone. By an oversight, the fact of the production of oxalic acid from naphthalene was not mentioned in the original article, although its isolation and analysis were given at length in the original notes. In the case of cymene, the oxalic acid is enclosed in brackets to indicate that it was not isolated. The cymene was examined immediately after nitration, the toluene and xylene not until after several months, during which long interval an opportunity had been afforded to the oxalic acid to separate in crystals.

The new oxygen derivative, C_6H_4O, obtained from benzene, *is not quinone*, $C_6H_4O_2$. Although in a brief abstract of my first article published in the *Berichte der deutsch. chem. Gesellschaft*, **13**, 1993, this substance is stated to be quinone, yet this statement is incorrect. It is expressly mentioned in my original paper, that the composition and the properties of the new substance conclusively establish that it is not quinone, but a monoxy-derivative of benzene.

The most striking phenomenon connected with the action of hyponitric anhydride upon the aromatic compounds, is the absence of uncombined water from among the products, and the formation of hydroxylated derivatives. The introduction of the hydroxyl group, in fact, is to be looked upon as the principal function of hyponitric anhydride in these cases. It is to be regarded, therefore, as an agent of quite a different sphere of application from nitric acid, which, under like circumstances, together with a certain amount of oxidation, acts chiefly by the introduction of the NO_2 group, water being eliminated. Not water, but nitrous oxide, N_2O, is given off when hyponitric anhydride is employed. No nitric oxide was found in the gas after it had acted upon the compound (benzene was the body more especially experimented upon in this connection), while *laughing gas was given off in great abundance.* This fact, together with the occurrence of the water of crystallization in the crystallized oxalic acid, which very slowly separated out of the mother liquid, is to be borne in mind in attempting to obtain, in a chemical equation, the numerous products actually formed. In the case of benzene, the following equation would be in harmony with what was actually observed:

$$6C_6H_6 + 13N_2O_4 = 3(C_2H_2O_4.2H_2O) + C_6H_4O + C_6H_5(NO_2) + C_6H_5.OH + C_6H_2(NO_2)_3.OH + 6CO_2 + 7N_2O.$$

When nitric acid acts upon benzene, the reaction takes place in accordance with the familiar equation :

$$C_6H_6 + HNO_3 = C_6H_5(NO_2) + H_2O.$$

But the liberation of N_2O, when N_2O_4 acts upon the aromatic compounds, shows that a decomposition must occur represented by

$$N_2O_4 = N_2O + O_2 + O.$$

In other words, the fact that an uneven number of atoms of oxygen is set free shows that at the moment of their liberation, one at least of these atoms must be in its uncombined or nascent condition. And while it has been abundantly demonstrated that triatomic oxygen cannot oxidize the elements of water into the form of hydroxyl, it has been conclusively shown that nascent or monatomic oxygen can. This is strikingly shown in the oxidation of phosphorus in the presence of water, where the nascent oxygen necessarily set free in the course of oxidation of the phosphorus, not only oxidizes the oxygen present into ozone, but a portion of the water into hydrogen peroxide. So, likewise, if benzene be added to the water in which the phosphorus is undergoing oxidation in partial oxidation with air, the ozone reaction disappears, and under proper conditions a notable amount of phenol is formed. The details of this experiment will presently be made public.

The sequence of decompositions resulting from the action of hyponitric anhydride upon benzene would appear to be as follows :

(1.) $3C_6H_6 + 2N_2O_4 = 2C_6H_5(NO_3) + C_6H_5.OH + N_2O + H_2O + O.$

(2.) $C_6H_6 + O + O = C_6H_4O + H_2O.$

The water thus found appears to have been that essential to the formation of the crystallized oxalic acid. No uncombined water, as previously stated, was found among the products of the reaction.

The phenol was at once and entirely converted into picric acid, a change established by an independent research upon the deportment of phenol itself with hyponitric anhydride.

So likewise in the treatment of the toluene, no less than three hydroxyl derivatives were produced—benzoic acid, the new modification of dioxybenzoic acid, and orcine, which was afterwards converted into the β-dinitro-orcine. In other words, we have in the first case the conversion of the side chain into carboxyl; in the second, this conversion along with the replacement of two hydrogen atoms of the nucleus by hydroxyl; in the third, the side chain is unaffected, and only the two hydrogen nucleus atoms have suffered replacement.

Similarly the xylene lost not only one of its two methyl groups, forming paratoluic acid, but also both of the members of the side chain with the production of phthalic acid. In the case of cymene, however, the propyl group appeared to break down so much more readily than the methyl group, that the latter was protected from the oxidizing action, and the only hydroxylated derivative was paratoluic acid. But the most striking exemplification of this tendency to form hydroxyl derivatives was exhibited by naphthalene. Not only was the carboxyl group produced, with the generation of phthalic and oxalic acids (both of which changes might be looked upon as evidence of a similarity of action between hyponitric anhydride and nitric acid), but the new hydroxylated compound, tetroxynaphthalene, $C_{10}H_4(OH_4)$, was formed. In this body no less than four of the hydrogon atoms in naphthalene are replaced by hydroxyl. At the same time, the diquinone, $C_{10}H_4O_4$, was formed, in which four atoms of hydrogen are replaced by oxygen.

It is not improbable that both dioxynaphthalene, $C_{10}H_6(OH)_2$, and naphthoquinone, $C_{10}H_6O_2$, were first formed and afterwards converted into these higher derivatives. But of these, and of naphthol and of dioxynaphthoquinone, $C_{10}H_4O_2(OH)_2$, no evidence could be found in the final products.

XLVI.—Detection of Starch Sugar Mechanically Mixed with Commercial Cane Sugar.

By P. Casamajor.

[Second Paper.]

In a previous communication on the same subject,* read before the American Chemical Society at the meeting of March, 1880, I gave several processes for the detection of starch sugar in commercial sugars. One of these consisted in adding to the suspected sugar a quantity of cold water, somewhat less than its own weight, and stirring the mixture for a few seconds. If starch sugar is present, it will be seen in the shape of white chalky specks.

Quite lately a sample of yellow refined sugar was given to me which was supposed to be adulterated by being mixed with starch glucose. By applying the test just mentioned, there seems to be left a few small chalky specks, which dissolved after standing a minute or two, making it very uncertain whether any starch glucose was present. Upon repeatedly trying the same test, the result was always doubtful.

* Journal of the American Chemical Society, **2**, 111.

I was then led to treat the suspected sugar by a liquid capable of dissolving sugar, but without any solvent action on starch glucose. After many trials, I found that methylic alcohol of such density as to mark 50° by Gay Lussac's alcohometer, answered the purpose very well, if previously saturated with starch sugar, as this solution dissolves cane sugar, either white or yellow, very readily, but does not dissolve starch glucose.

Methylic alcohol at 50°, saturated with starch sugar, gives a solution of specific gravity = 1.25. 100 c.c. of methylic alcohol at 50° dissolves 57 grms of dry starch sugar, the volume of the solution being 133 c.c. A solution of starch sugar in ethylic alcohol does not answer so well, because ethylic alcohol does not dissolve so readily the gummy matters found in soft sugars, which are those generally chosen for adulteration with glucose.

To test the presence of starch sugar in a commercial cane sugar, the suspected sugar should, in the first place, be thoroughly dried, as otherwise any water present will weaken the alcohol, and enable it to dissolve more starch sugar. It should then be stirred for about two minutes with the saturated solution of starch sugar in methylic alcohol. After this, the residue is allowed to settle, and the clear solution poured off. The residue may then be washed with a fresh quantity of the same solution. After stirring again and allowing the residue to settle, there will remain, if any starch sugar is present, a certain quantity of chalky white specks, accompanied by a fine deposit, formed by the starch sugar present, in powder or fine grains. These finer particles are never seen when water is used for detecting the presence of starch sugar, as they dissolve in water very readily. It seems probable that by using this solution of starch sugar in weak methylic alcohol, the starch sugar in an adulterated sample could be estimated quantitatively by a process somewhat analogous to that of Payen for estimating cane sugar.

Not having had any occasion for such a process, I have not determined experimentally the degree of approximation obtainable in this way.

The methylic solution of starch sugar should be poured on a filter, after it has dissolved all it can from a commercial sugar, and the residue should be washed out with the same solution, and everything poured on a weighed filter. After all the liquid has run off, the filter and the residue may be rapidly washed with the strongest methylic alcohol found in commerce, which tests 92½° by Gay Lus-

sac's alcohometer, and which dissolves starch sugar with great difficulty.

By a dexterous use of this process, it seems probable that very approximate results may be obtained, although what is said here is merely in the nature of a suggestion to those who may have use for quantitative results.

Abstracts from American and Foreign Journals.

Bulletin de la Société Chimique de Paris.

Abstractor, E. H. S. BAILEY, Ph.B.

On the Sulphocyanate of Platinum of M. Marcano, G. WYRONBOFF (**33**, 402).—The body described by M. Marcano (*Bull. Soc. Chim. de Paris*, **33**, 250) is not a sulphocyanate of platinum, $(CyS)_8Pt$, but rather a sulphoplatinate of potassium, $(CyS)_6PtK_2$, a body previously described.

A Combination of Tetrachloride of Titanium and Chloride of Acetyl, A. BERTRAND (**33**, 403).—By mixing tetrachloride of titanium with chloride of acetyl, yellow octahedral crystals are obtained, having the symbol $C_2H_3OCl + TiCl_4$.

Some Properties of Mixtures of Cyanide of Methyl with Ordinary Alcohol and with Methyl Alcohol, C. VINCENT and B. DELACHANAL (**33**, 405).—This subject is discussed under the topics:

1. Boiling point of mixtures of alcohol and cyanide of methyl.
2. Density of the preceding mixtures.
3. A method for the separation of cyanide of methyl from ordinary alcohol.
4. Boiling point and density of mixtures of methyl alcohol and cyanide of methyl.

On the Determination of Urea by Hypobromite of Sodium, C. MÉHU (**33**, 410).—Will be noticed elsewhere.

Oxalic Acid, A. VILLIERS (**33**, 415).—Fine crystals of normal oxalic acid, $C_4H_2O_8$, can be obtained by dissolving, with the aid of heat, small quantities of ordinary oxalic acid in concentrated sulphuric acid. After some time crystals are deposited which are in the form of right octahedrons with rhombic base, and are very transparent. Ordinary hydrated oxalic acid crystallizes in clinorhombic prisms. A number of other characteristics of the normal acid are also noticed.

Electrolysis of Malonic Acid, E. BOURGOIN (**33**, 417).—From the experiments made, the following characteristics of malonic acid are deduced :

In a free state, it is possessed of considerable stability when acted upon by the electric current and becomes gradually more concentrated at the positive pole. These characteristics distinguish it from its lower homologue, oxalic acid.

In a concentrated alkaline solution, no hydrocarbon is in any case set free. This distinguishes it from succinic acid. These differences are such that if free methylene had not to the present time been undiscovered, we should be tempted to believe that the malonic acid of synthesis is not a true homologue of oxalic and succinic acids.

Acetobenzoic Anhydride, W. H. GREENE (**33**, 424).—The experiments of M. Loir in regard to the properties of acetobenzoic anhydride, described in *Bull. Soc. Chim. de Paris*, **32**, 164, have been repeated by the author. He concludes that there is no difference between the benzoate of acetyl and acetate of benzoyl. In whatever way they are made their constitution and reactions, in the same conditions, are identical.

The Constitution of Salts of Rosaniline and of Analogous Coloring Matters, A. ROSENSTIEHL (**33**, 342 and 426).—This is an exhaustive discussion in which two questions are examined. The first is general in regard to the chemical cause for the coloration of these bodies ; the other is special and refers particularly to the constitution of rosaniline. It is shown that there can be coloration without supposing a double union between one of the atoms and the rest of the molecule. This union is at least an unverified hypothesis. This fact has been lost sight of by some who have used it as a basis of demonstration. If it is simply an hypothesis, it is not necessary to introduce it into the formula of rosaniline.

On the Resin of Palissandre Wood (Purple Ebony), A. TERREIL and A. WOLFF (**33**, 435).—This resin is extracted with alcohol. It is readily soluble in chloroform, carbon disulphide, fixed alkalies and conc. sulphuric acid. An analysis shows it to have a composition nearly corresponding to the formula, $C_{21}H_{21}O_6$.

Mineral Waters Containing Iron and Nitrates, ED. WILLM, (**33**, 450).—Analyses of a number of waters are given in detail.

The Waters of Bourboule, A. RICHE (**33**, 452).—The arsenic, which is a notable constituent of these springs, has not altered in

quantity in two of them. In two others it appears to be slowly decreasing.

Preparation of Acetonitrile, E. DEMARÇAY (**33,** 456).—By the distillation of acetamide there is obtained at first ammonia, water and acetonitrile, and afterwards water, acetonitrile and a little acetic acid. From these facts it is evident that if acetamide be heated somewhat above its boiling point, it will be decomposed into acetonitrile and water, that the water thus produced decomposes a little acetamide into ammonia, which escapes, and acetic acid, which nearly all remains. When a certain quantity of acetic acid is present, this last reaction does not take place, but simply water and acetonitrile are formed.

Advantage may be taken of this reaction to obtain acetonitrile in large quantities. Acetamide is heated with crystallizable acetic acid, observing proper precautions, and the distillate is dried over potassic carbonate.

A new Method for Making Acetal, R. ENGEL and DE GIRARD (**33,** 457).—To produce acetal a current of hydrogen phosphide is passed through a cooled solution of aldehyde, in a little more than its own volume of absolute alcohol, for three days. From this mixture water causes a liquid to separate which, upon fractional distillation, gives off, at 102°, a substance which is proved to have all the properties of acetal.

On the Commercial Analysis of Bituminous Rocks, P. KIENLERO (**33,** 459).—Will be noticed elsewhere.

Borotungstates, DANIEL KLEIN (**33,** 466).—By boiling together equal weights of tungstic hydrate and pentametaborate of potassium ($Bo_5O_{10}KH_4 + 2Aq$) crystals are readily obtained, which on analysis show a composition corresponding to the formula,

$$2K_2O,12TuO_3,Bo_2O_3 + 15Aq.$$

Another salt described is borodecitungstate of barium,

$$10TuO_3,B_2O_3,2BaO + 20\ Aq.$$

Action of Water on Zinc Tanks and Lead Pipes, X. ROCQUES (**33,** 499).—Zinc, lead and copper are attacked very slowly by ordinary water, and by ordinary saline solutions (chlorides and bicarbonates).

The action is more intense when several metals are in contact, because magnetic force is added to chemical force. The presence of nitrogenous matter and ammonia intensifies the action, especially when in contact with zinc.

These phenomena have their maximum intensity where most oxygen is present. This is particularly the case on the surface of a reservoir, or where there is alternate contact with air and with water. A deposit in the bottom of some tanks contained oxides of zinc, lead and copper. A deposit in a reservoir, connected with lead pipes, contained 0.027 per cent. of carbonate of lead. Iron pipes are to be recommended as a substitute for lead.

On the Heat of Formation of Ammonia, BERTHELOT (**33**, 505).—After discussing and pointing out the errors of previous determinations, the author gives the results of a method which consisted in burning the ammonia gas in free oxygen. By this process the numbers + 21.0 cal. and + 12.2 cal. are obtained for ammonia solution and for the gas.

The Heat of Formation of Oxides of Nitrogen, BERTHELOT (**33**, 509).—It is possible that errors have crept into the methods of previous experimenters, because the heat has been determined very indirectly. In any determinations where the heat of formation of ammonia is a factor, the results must be modified by the data obtained in the article above. A new series of experiments has been devised in which a steel detonating vessel was used. Binoxide of nitrogen is exploded in this with a proportional quantity of cyanogen or ethylene. The heat of combustion of cyanogen and of ethylene in oxygen are also determined. From these data the heat of formation of binoxide of nitrogen is found to be 21.6 ; combustion of oxide of carbon in oxygen and in protoxide of nitrogen gives 10.3 for CO. A corrected table for the thermic formation of oxides of nitrogen, of nitrates and of ammoniacal salts, is also given.

Observations in Reference to a Note of Messrs. Vincent and Delachanal regarding Pure Cyanide of Methyl, A. GAUTIER (**33**, 515).—A reclamation of priority.

Researches on the Determination of Heavy Mineral Oils and Resin of Fatty Oils and Resin in Commercial Oils, A. RÉMONT (**33**, 461 and 525).

Chemical Stability of Matter under the influence of Sonorous Vibrations, BERTHELOT (**33**, 547).—It is a well known fact that sudden shocks will produce chemical combination. In order to ascertain whether similar effects will be produced by sonorous vibrations, various substances, as ozone and oxygen, arsenic and hydrogen, ethylene and sulphuric acid, and also hydric peroxide, and persulphuric acid were connected with an apparatus whereby they were

subjected to vibrations of 100 per second and of 7,200 per second. No sensible effect was produced. It seems, therefore, that matter is stable under the influence of sonorous vibrations, but is readily affected by ethereal vibrations. In this connection it is worthy of note that the vibrations of heat and light waves are infinitely more rapid than those of sound waves.

On the Preparation of Ashes used for the Extraction of Iodine from Marine Plants called Seawrack, Dr. THIERCELIN (**33**, 559).—An extended description is given of the method of collecting the seaweed, drying, fermentation, and incineration. This is also accompanied by a description of the furnace used in the latter operation.

Manufacture of Phosphoric Acid, A. COLSON (**33**, 563).—The natural, unground phosphate is digested in dilute hydrochloric acid for about twenty-four hours; the clear solution is decanted off, and the residue washed with water. This wash water is used to dilute another lot of acid. The acid solution is mixed with enough sulphuric acid of 50° B. to precipitate all the lime. The sulphate of lime is then separated by pressure, the acid liquid is concentrated, and the hydrochloric acid evaporated off and condensed in towers. A solution is thus obtained containing 400 to 500 grms of phosphoric anhydride per liter, with some hydrochloric acid also.

On the Complex Acids containing Boric Acid, Dr. FRANCESCO MAURO (**33**, 564).—These researches cover nearly the same ground as those described by M. Klein (*Bull. Soc. Chim.*, **33**, 466).

The Combination of Tetrachloride of Titanium with Protochloride of Phosphorus, A. BERTRAND (**33**, 565).—By mixing solutions of tetrachloride of titanium with protochloride of phosphorus, small crystals are obtained which melt at 85°.5. They have a composition corresponding to the formula, $TiCl_4,PCl_3$, and are acted upon by ammonia in accordance with the equation:

$$TiCl_4,PCl_3 + 9(NH_4,OH) = TiO_2 + PO_3(NH_4)_2H + 7NH_4Cl + 4H_2O.$$

Combination of Tetrachloride of Titanium with Oxide of Ethyl, A. BERTRAND (**33**, 566).—If the vapors of ether are mixed with those of tetrachloride of titanium, fine yellowish-green crystals are produced.

Reduction of Nitrate of Ethyl by Alcohol, A. BERTRAND (**33**, 566).—If a solution of nitrate of silver in absolute alcohol is treated with iodide or bromide of ethyl, iodide or bromide of silver is precipitated, $AgNo_3 + C_2H_5I$ or $C_2H_5Br = AgI$ or $AgBr$. But the alco-

holic solution does not yield nitrate of ethyl. Some oxide of ethyl distils over, and from that portion coming over below 70°, nitrite of ethyl and aldehyde are obtained in accordance with the reaction:

$$C_2H_5NO_3 + C_2H_5OH = C_2H_5NO_2 + C_2H_4O + H_2O.$$

Substances contained in the Coke from Petroleum, L. PRUNIER and EUG. VARENNE (**33**, 567).—The authors have treated petroleum coke with various solvents. By acting upon it with bisulphide of carbon, they obtained an insoluble residue containing some sulphur and about 98 per cent. of carbon, and by evaporating the bisulphide of carbon solution, a product containing about 94 per cent. of carbon. This latter was treated successively with alcohol, ether and crystallizable acetic acid, and in the residue insoluble in these, but dissolved in bisulphide of carbon, the hydrocarbon $(C_{14}H_2)_n$ was obtained. The original bisulphide of carbon solution gave, upon fractional distillation, hydrocarbons having from 97.7 to 98.11 per cent. of carbon. The experiments tend to confirm the theories of Berthelot previously announced. In these compounds it will be noticed that the percentage of carbon is always very high, and the molecular weight constantly increasing.

Preparation of Malonic Acid, E. BOURGOIN (**33**, 572).—After numerous experiments upon methods previously described the author recommends the following synthetical method: A solution of monochloracetic acid, in double its weight of water, is saturated with a solution of potassic bicarbonate, some pure potassic cyanide is added, and the solution is slowly heated on a water bath. After the ebullition, attendant upon the combination, has ceased, double the volume of conc. hydrochloric acid is added, the precipitated potassic chloride is removed, hydrochloric acid gas is passed through the liquid, and the precipitated salts are again removed. The acid solution is then evaporated in a water bath to dryness, and from an ethereal solution of this mass perfectly pure malonic acid separates on evaporation. This process is easy of execution, and yields almost the theoretical amount of acid.

On the Heat of Formation of Gun-cotton, SARRAU and VIEILLE (**33**, 581).—The substance experimented upon is a mixture of bi- and trinitrocellulose, and was decomposed at different pressures, varying from 100 atmospheres to 6,000. The heat of combustion is not a constant quantity. Only the heat of formation can give data independent of the conditions of the experiment. The numbers found are, 542 calories per kgrm of this complex molecule, and 640 for its equivalent.

Isomeres of Phloroglucine, A. GAUTIER (**33**, 582).—From a study of many vegetable substances, it is noticed that there is a tendency to dehydration of the glucosides, and a decomposition into saccharine bodies and aromatic substances. It may be possible also that dehydration of these different saccharine substances which go to make up the original glucoside, will give different triatomic phenols. The name *glucines* has been adopted by the author for a series of bodies, $C_6H_6O_3$, which have different properties from phloroglucine. Among those investigated are œnoglucine and quercigluc ine, the former derived from the coloring matter of wines, and the latter from quercitron by fusion with alkalies.

Action of Monobromodiphenylmethane upon Ammonia, C. FRIEDEL and M. BALSOHN (**33**, 587).—When monobromodiphenylmethane is acted upon by a cold alcoholic solution of ammonia, bromohydrate of ammonia separates out, and from the alcoholic solution, by the addition of water, the mixed ethylbenzhydrolic ether is obtained.

If a conc. aqueous ammonia solution is used in place of an alcoholic solution, the crystals of bromide being dried and placed in contact with an excess of ammonia, they are gradually decomposed and after some time contain no more bromodiphenylmethane. From this solid mass, dissolved in alcohol and crystallized, the secondary amine derivative of diphenylmethane is obtained:

$$2(C_6H_5)_2 = CHBr + NH_3 = (C_6H_5)_2 = (CH)_2NH + 2HBr.$$

From the alcoholic mother liquor, the primary amine is obtained, viz: $(C_6H_5)_2 = CHNH_2$. If the hydrocarbon of benzhydrol be called benzhydrol, these two amines may be called benzhydrolamine and dibenzhydrylamine.

Synthesis of Diphenylacetic Acid, C. FRIEDEL and M. BALSOHN (**33**, 589).—A new method for the synthesis of this acid is to heat at 165° for eighteen hours, monobromodiphenylmethane with two-thirds its weight of cyanide of mercury. The mass is then acted upon by benzene and by water. The benzene solution, after being decanted, is distilled and gives a product which is treated with alcoholic potassa, agitated with water and ether; and after decantation of the ether the aqueous solution is heated to drive off the dissolved ether, hydrochloric acid is added, and the diphenylacetic acid thus precipitated is purified by recrystallization. The purified product melts at 148°.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office**, by ARNO BEHR.

Nov. 9, 1880.

234,129.—*Production of sulphur, copper-matte, etc., from pyrites.* JOHN HOLLWAY.

A blast of air is forced through the molten mass, the heat developed herein is utilized in melting down a subsequent charge of ore, after which the volatile products are conducted into a collecting chamber, where the sulphur and the condensable sulphides or oxides are deposited.

234,142-144.—*Process of and apparatus for preparing wool for making paper pulp.* WM. R. PATRICK.

This is essentially an alternate treatment of the wool with water and steam under pressure.

234,145.—*Manufacture of bichromates.* HENRY PEMBERTON.

Carbonic acid gas is passed into the calcined mixture.

234,168 and 234,169.—*Pyrometer.* EDWARD BROWN.

234,190.—*Method of generating artificial heat.* BENJAMIN N. HUESTIS.

Claims "burning petroleum in connection with a bed of calcium (sic) or of common lump lime saturated with the oil."

Nov. 16, 1880.

234,400.—*Process of and apparatus for manufacturing illuminating gas.* ARTHUR O. GRANGER and JOSEPH H. COLLINS, JR.

Refers to the production of water gas, which is afterwards carburetted, the carburetting fluid hydrocarbon being transformed into a fixed gas.

234,413.—*Galvanic battery.* GEORGE L. LECLANCHE.

234,425.—*Roofing composition.* CHRISTOPHER F. PEARSON.

Yellow ochre, whiting, litharge, india-rubber and linseed oil.

234,428.—*Compressed malt.* ROBERT PRENDERGAST and ROBERT FREE.

The malt is crushed and then compressed to form coherent blocks.

234,442.—*Roofing and paving material.* CYRUS M. WARREN.

234,482.—*Alloy for coating metals.* JOHN B. JONES.

An alloy of nickel, lead, tin and zinc.

234,489.—*Explosive compound.* CHARLES A. MORSE.

The solutions of nitroglycerine and resin in some volatile solvent are mixed, and the solvent removed by evaporation.

234,494.—*Preparations melting under 32° F.; apparatus therefor, and their application.* STANISLAS H. ROUART.

"Solid ice enclosing particles of salt."

234,510 and 234,511.—*Treatment and preparation of saccharine substances.* MORIZ WEINRICH.

Refers to the preparation and purification, by washing with alcohol, of a saccharate of lime from molasses.

234,524.—*Coating iron with oxide.* GEORGE and ANTHONY S. BOWER.

The iron is treated at a high temperature with carbonic acid.

234,567.—*Compound for preserving animal and vegetable substances.* JULIUS HAUFF.

A dry preserving compound, consisting of borax and boracic acid.

234,595.—*Manufacture of ferric oxide and cupric chloride.* JUAN F. N. MACAY.

In the presence of air, cupric oxichloride and a solution of ferrous chloride react upon each other, and produce the substances referred to in the Patent.

Nov. 23, 1880.

234,675.—*Composition for coating surfaces.* CHARLES M. JACOB.

A varnish consisting of collodion, creosote, boiled linseed oil, black oxide of manganese and rosin.

234,680.—*Liquid starch polish compound.* SANTIAGO LIMA.

Water, borax, tallow, cotton-seed oil, gelatine and castor oil.

234,704.—*Manufacture of white aluminous cake.* GEORGE F. BIHN.

The product of the reaction of sulphuric acid on a mixture of halloysite and bauxite, is treated in a semi-fused state with alkaline sulphites or bisulphites.

234,737.—*Fire-proof compound for furnace-linings, converter-bottoms, tuyeres, etc.* ERNST F. ALTHAUS, OTTO JUNGHAUS and HERMANN UELSMANN.

A mixture of dolomitic lime and caustic alkali, or alkaline carbonates.

234,782.—*Fertilizer.* BENJAMIN JOHNSON and WOOSTER P. GIDDINGS.

Ground unburned oyster shell, potash and soda.

234,789.—*Manufacture of iron and steel.* ALFRED KRUPP.

A charge of molten iron is allowed to remain on the hearth in contact with oxide of iron until phosphorus, sulphur and silicon have been taken up by the oxide, and when the carbon begins to burn is withdrawn into a second furnace for subsequent treatment, for the production of steel or puddled iron.

234,815.—*Process of extracting malt.* JOHN A. SCHAEFER.

234,838.—*Artificial stone.* GEORGE W. MASON.

Nov. 30, 1880.

234,844.—*Compound for curing and preserving meats.* WILLIAM ARCHDEACON.

Salt, pyroligneous acid and salicylic acid.

234,884.—*Apparatus for and process of separating gold, silver and copper from lead.* ARTHUR H. MEYER.

234,904.—*Apparatus for mixing aeriform fluids.* JOHN F. BARKER.

234,998.—*Apparatus for purification of the products resulting from distillation of wood.* JEAN A. MATHIEU.

235,014.—*Preparation of clay for manufacture of pottery.* SIMEON G. PHILLIPS.

The clay is soaked in a thin solution of alum.

235,053.—*Manufacture of starch.* THEODORE GASSAWAY.

Refers to the manufacture of starch from wheat, without fermentation.

235,057.—*Process of refining paraffine wax.* WILLIAM M. SLOANE and WILLIAM BELL.

It is recrystallized from naphtha, pressed, melted and filtered.

Foreign Patents.

Condensed from R. BIEDERMANN's Report to the German Chemical Society, by OTTO H. KRAUSE.

R. GRUENEBERG, Alt Damm: *Improvements in the method of preparing potassium sulphate from Stassfurt salts.* (Germ. P., No. 10753, September 13, 1879.)—Schoenite, which is subsequently converted into potassium sulphate, is formed by bringing together potassium chloride and magnesium sulphate, and the resulting liquors used for dissolving natural or artificial carnallite, or kainite. (See preceding Patent.)

H. PRECHT, New Stassfurt: *Method of separating sodium and magnesium chloride from potassium-magnesium sulphate, derived from kainite.* (Germ. P., No. 10637, August 5, 1879.)—Kainite is treated under a steam pressure of 2–5 atmospheres, with water or saline solutions, magnesium sulphate excepted, in quantities of the solvents insufficient for the solution of the sodium chloride.

M. NAHNSEN, Leopoldshall: *Method of working up kainite.* (Germ. P., No. 10772, February 26, 1880.)—Water and hydrochloric acid are driven off by heating to redness. The resulting friable mass, consisting of magnesia and potassium and magnesium sulphate, is treated with a saturated solution of sodium chloride, to remove mechanically the rock salt which remains unaltered during the heating; magnesia is left as a residue upon treatment of the double sulphates with water.

B. BERNHARDI, Stassfurt: *Improvements in the method of treating saline lyes containing potassium compounds.* (Germ. P., No. 10821, December 18, 1879.)—Magnesium sulphate, in dry form or in solution, is added to the mother liquors resulting from working up carnallite, schoenite, or potassium chloride.

HENRY GLOVER, Silvertown: *Method and apparatus for manufacturing and concentrating sulphuric acid.* (Germ. P., No. 10834, March 26, 1880.)—The object of this invention is to prevent loss of sulphur by sublimation, in burning sulphur, or pyrites, and to utilize completely the heat of combustion. The gases from the furnace are made to pass through a chamber containing open brick work, like in a hot blast stove, in which the volatilized sulphur deposits. When the chamber has become hot enough, air is admitted from a flue beneath, and the sulphur burned away. Over these chambers, platinum vessels of peculiar construction are placed for concentrating the acid, and thereby utilizing the heat.

I. V. RICKMAN, London, and I. B. THOMPSON, New Cross: *Method and apparatus for generating ammonia.* (Germ. P., No. 10889, March 11, 1880.)—Carbonaceous materials are subjected to slow combustion upon an inclined grate by limiting the supply of air and steam. The ammonia is absorbed from the products of combustion by means of acids. Or the materials may be moistened with 4–8 per cent. of sodium chloride, and burned in a coke oven, and the ammonia obtained as chloride. (The utilisation of atmospheric nitrogen in this or a similar manner, has been previously attempted by Rickman, Engl. P., No. 3348, 1878, and by others before him; among others, Swindell's Engl. P. of June 21, 1876. R. B.)

G. J. WELLS, Widnes: *Manufacture of caustic alkalies.* (Engl. P., No. 3803, September 22, 1879.)—Alkaline carbonates are treated with lime in the cold and under pressure.

W. J. MENZIES, St. Helens: *Manufacture of caustic alkalies.* (Engl. P., No. 3804, September 22, 1879.)—Similar to the above. The solution of alkaline carbonate is treated under pressure in a close vessel, having a false bottom, upon which a layer of limestone is placed to serve as a filter.

MR. PAULI, Mannheim: *Improvements in firing balling furnaces.* (Engl. P., No. 3825, September 23, 1879.)—Produces generator gas upon the grate of the furnace, and burns it within the revolving cylinder.

G. I. B. LACOMBE, Lille: *Treatment of soda and potash.* (Engl. P., No. 3661, September 13, 1879.)—Employs Leblanc's process for preparing cyanides and ferrocyanides, by heating a mixture of potassium sulphate, chalk, coal, ferric oxide and nitrogenous organic matter. The fused mass is extracted with water, and the liquid treated with carbonic acid, etc.

W. CHADWICK, T. CHADWICK and J. CHADWICK, Manchester: *Manufacture and purification of aluminium sulphate.* (Engl. P., No. 4078, October 9, 1879.) Pulverized bauxite is mixed with 3–5 per cent. of its weight of arsenious acid, and dissolved in sulphuric acid. Iron in combination with arsenious acid, is precipitated as a brown precipitate, upon the addition of lime to the diluted liquid. Excess of arsenious acid is removed from the filtrate by means of hydrogen sul

phide. If use of arsenic is to be avoided, the bauxite may be mixed with 10 per cent. of oxalic acid and 5–10 per cent. of hydrochloric acid, to remove iron and lime.

BADISCHE ANILIN UND SODAFABBIK, Mannheim : *Method of preparing nitrosulphonic acids of alpha-naphthol, and particularly dinitronaphthol-sulphonic acid.* (Germ. P., No. 10785, December 28, 1879.)—If the attempt be made to nitrate naphtholmonosulphonic acid, dinitronaphthol is produced. Higher naphtholsulphonic acids, however, and especially naphtholtrisulphonic acid, can be nitrated. Ten kgrms alpha-naphthol are treated at 40–50° C., with 20 kgrms fuming sulphuric acid containing 25 per cent. anhydride, until naphthol ceases to separate upon dilution ; 18 kgrms fuming sulphuric acid of 70 per cent. anhydride are then added, and the heating continued. The end of the sulphuration is attained when a sample, after being nitrated, ceases to separate dinitronaphthol upon dilution with water.

HÖRDER BERGWERKS UND HÜTTENVEREIN HÖRDER UND RHEINISCHE STAHLWERKE, Ruhrort. *Method of dephosphorizing iron.* (Germ. P., No. 10472, September 10, 1879.)—Object of this invention is to remove the phosphorus before all the carbon is removed from the iron in the Bessemer process. For this purpose tribasic calcium and magnesium phosphates are formed, and these rendered fusible and suitable for being taken up by the slag, by the addition of fluor spar.

THE AMERICAN CHEMICAL SOCIETY.

XLVII.—Proceedings.

Annual Meeting, Thursday, Dec. 2d, 1880.

Dr. E. R. Squibb in the chair.

Minutes of previous meeting read and approved.

Minutes of the meeting of Directors read.

The Librarian stated that he had not been able to prepare his annual report in time for this meeting.

Dr. S. A. Goldschmidt reported on behalf of the Curators the receipt of the case of dye-stuffs from Messrs. Pickhardt and Kuttroff.

After which the election of officers for the year 1881 took place, Messrs. Casamajor and Alsberg being appointed tellers by the Chairman. The following officers were declared duly elected:

President:

Chas. F. Chandler.

Vice-Presidents:

1. A. R. Leeds,
2. E. R. Squibb,
3. Henry Morton,
4. G. A. Koenig,
5. C. A. Goessmann,
6. Ira Remsen.

Corresponding Secretary:

P. Casamajor.

Recording Secretary:

Albert H. Gallatin.

Treasurer:

W. H. Nichols.

Librarian:

E. Waller.

Curators:

Wm. Rupp, A. J. Rossi, A. A. Fesquet.

Committee on Papers and Publications:

ARNO BEHR, GIDEON E. MOORE, A. R. LEDOUX.

Committee on Nominations:

WILLAM GEYER, O. KRAUSE,
JAS. H. STEBBINS, ARTHUR H. ELLIOTT,
J. C. BATTERSHALL.

Board of Directors:

A. R. LEEDS,
E. R. SQUIBB,
H. MORTON. } Three Local Vice-Presidents.

P. CASAMAJOR, C. F. CHANDLER,
ALBERT H. GALLATIN, H. MORTON,
W. H. NICHOLS, W. M. HABIRSHAW,
E. WALLER, M. ALSBERG,
A. R. LEDOUX. J. GOLDMARK.

A notice was then given that at the next meeting a motion will be made to amend By-law No. 5; that the dues of resident members be reduced to five dollars per annum.

After which the following gentlemen were unanimously elected: As members:

ALBERT C. HALE, State School of Mines, Golden, Colorado,
Nominated by { C. F. CHANDLER, ARTHUR H. ELLIOTT, ALBERT R. LEEDS.

NARCISSE PIGEON, 128th street and 4th avenue, N. Y. City.
Nominated by { C. F. CHANDLER, ARTHUR H. ELLIOTT, ALBERT R. LEEDS.

THEODORE LUNGWITZ, Jersey City, N. J.
Nominated by { H. E. NEISE, O. H. KRAUSE, ARNO BEHR.

BYRON N. WITTMANN, Reading, Pa.
Nominated by { E. H. S. BAILEY, GIDEON E. MOORE, H. ENDEMANN.

HENRY J. SEEMAN, Crane Iron Co., Catarauga, Pa.
Nominated by { E. H. S. BAILEY, GIDEON E. MOORE, H. ENDEMANN.

CHAS. W. SCHMICH, Rockhill Iron & Coal Co., Arbisonia, Huntington Co., Pa.

Nominated by { E. H. S. BAILEY, GIDEON E. MOORE, H. ENDEMANN.

Dr. HENRY FRIEDBURG.

Nominated by { P. CASAMAJOR, H. ENDEMANN, E. R. SQUIBB.

As associate members:

HERMAN T. VULTÉ, School of Mines, N. Y.

Nominated by { ARTHUR H. ELLIOTT, C. F. CHANDLER, ALBERT R. LEEDS.

T. G. WIECHMANN, School of Mines, N. Y. City.

Nominated by { ARTHUR H. ELLIOTT, C. F. CHANDLER, ALBERT R. LEEDS.

T. D. O'CONNOR, School of Mines, N. Y. City.

Nominated by { ARTHUR H. ELLIOTT, C. F. CHANDLER, ALBERT R. LEEDS.

CHAS. KYLE, Jr., 3 East India Ave., London E. C., England.

Nominated by { W. H. NICHOLS, ARTHUR H. ELLIOTT, C. F. CHANDLER.

The following gentlemen were nominated:

Dr. H. GERBER, 45 S. Washington square, N. Y. City.

Nominated by { H. ENDEMANN, A. BEHR, JAS. H. STEBBINS, Jr.

Prof. F. P. VENABLE, Chapel Hill, North Carolina.

Nominated by { J. W. MALLETT, C. F. CHANDLER, ARTHUR H ELLIOTT.

Resignation of JOHN P. MARSHALL was read and accepted.

After which the following papers were read:

1. "On some New Azo Colors." By JAS. H. STEBBINS, Jr.

2. "On Wilkinson's Process for the Manufacture of Illuminating Gas from Wood." By Prof. CHAS A. DOREMUS.

The following papers were read by title:

1. "On Para and Orthotolylsulphomethane." By C. LIEBERMANN and L. LINDERMANN.

2. "On Compounds of Anthracene with the different Oxides of Nitrogen." By C. LIEBERMANN and L. LINDERMANN.

3. "On the Composition of Aesculine and Aesculetine." By C. LIEBERMANN and R. KNIEBREK.

4. "Investigations on the Reduction of Anthraquinone." By C. LIBERMANN.

5. "On the Electrolytic Determination of Silver." By H. FRESENIUS and F. BERGMANN.

6. "On the electrolytic Determination of Nickel and Cobalt." By H. FRESENIUS and F. BERGMANN.

7. "On Cyanethine and new bases derived therefrom." By ERNEST VON MEYER.

After which meeting adjourned.

ARTHUR H. ELLIOTT,
Recording Secretary.

XLVIII.—SOME NEW AZO COLORS.

BY JAS. H. STEBBINS, JR.

For lack of time, the following paper will only give a brief account of some of the new dyes I have obtained within the last two months. Some of these compounds are pretty dyes, but possessing no material advantage over those in the market; others are merely interesting from a scientific point of view.

Among the first I will mention "Orange No. 3."

This pretty dye-stuff was obtained by diazotizing metanitraniline, and combining one molecule of the so obtained diazo-compound, with one molecule of beta-naphtholdisulpho acid, in an alkaline solution. Common salt precipitates the dye-stuff, in the form of a yellow paste. This is soluble in water in all proportions, and dyes wool in an acid bath, of a fine and clear orange color.

The reaction taking place here, may be expressed by the following terms:

Azometanitrobenzole-beta-disulphonaphthol,

$$C_6H_3\overset{3}{N}O_2 : \overset{1}{N} = N - \beta\text{-}C_{10}H_4(NaSO_3)_2OH.$$

We will next pass on to "Orange No. 4."

Produced by combining equal molecules of paradiazosulphoxylol and an alkaline solution of resorcine.

Hydrochloric acid precipitates the free acid in the shape of a red paste, which is easily soluble in water.

Formula: $C_6H_2(CH_3)_2\overset{4}{H}SO_3 - \overset{1}{N} = N - C_6H_3(OH)_2$.

In an acid bath, it dyes wool a sort of old gold color.

Parazosulphoxylnaphthalene-alpha-sulphoxylphenol,

$C_{10}H_6(\overset{4}{H}SO_3) - \overset{1}{N} = N - \alpha\text{-}C_6H_3(HSO_3)OH$.

Prepared by combining equal molecules of diazonaphthionic acid and phenolsulpho acid, in an alkaline solution.

The soda salt falls from the free acid by addition of NaCl, in the form of a yellow-brown paste which is easily soluble in water.

An excess of HCl decomposes the soda salt, regenerating the free acid.

Parazodimethyl-sulphoxylbenzole-alpha-naphthol,

$C_6H_2(CH_3)_2(\overset{1}{H}SO_3) - \overset{4}{N} = N - \alpha\text{-}C_{10}H_6OH$.

This brown dye is prepared by combining paradiazosulphoxylol with an alkaline solution of alpha-naphthol, equal molecules of each being taken. HCl precipitates the free acid in the shape of a dark brown, flocculent mass, which is easily soluble in water.

Similar to this compound in composition, but differing greatly in shade, is

Paradiazosulphoxylol-beta-naphthol,

$C_6H_2(CH_3)_2(\overset{4}{H}SO_3) - \overset{1}{N} = N - \beta\text{-}C_{10}H_6OH$.

If equal molecules of paradiazosulphoxylol and beta-naphthol, in an alkaline solution, are mixed together, a thick scarlet gelatinous precipitate is instantly formed. This precipitate is collected on a filter, dissolved in boiling water, and reprecipitated by means of common salt, in the shape of a soda salt.

The free acid is precipitated from a hot solution of the soda salt by means of HCl, and forms little microscopic star-grouped red needles, with a strong golden bronze lustre.

The soda salt is composed of little red leaflets, easily soluble in water.

The silver salt is composed of fine red needles, less soluble in water than the soda salt. Two silver determinations gave the following results:

Calculated for $C_6H_2(CH_3)_2(\overset{4}{Ag}SO_3) - \overset{1}{N} = N - \beta\text{-}C_{10}H_6OH$.

1. Ag ..... 19.36 per cent.
2. Ag ..... 19.93 per cent.

THEORY.

Ag.....23.11 per cent.

The low percentage of silver in these two analyses is probably due to some impurity in the silver salt, difficult to remove by the ordinary methods of purification.

Metazonitrobenzole-alpha-naphthol,

$$C_6H_4\overset{3}{N}O_2\overset{1}{N} = N - \alpha\text{-}C_{10}H_6OH.$$

Produced by treating diazometanitrobenzole with an alkaline solution of alpha-naphthol.

HCl throws down the free acid in the shape of a red-brown precipitate, soluble in water.

Parazosulphoxylxylol-β-phenanthrol,

$$C_6H_2(CH_3)_2(\overset{4}{H}SO_3)\overset{1}{N} = N - \beta\text{-}C_{14}H_8OH.$$

Prepared by treating paradiazosulphoxylol with an alkaline solution of beta-phenanthrol. HCl precipitates the free acid.

This red-brown dye dyes silk and wool in an acid bath.

Parazosulphoxylxylol-alpha-dibromnaphthol,

$$C_6H_2(CH_3)_2(\overset{4}{H}SO_3) - \overset{1}{N} = N - \alpha\text{-}C_{10}H_4(Br_2)OH.$$

Prepared by treating one molecule of paradiazosulphoxylol with one molecule of alpha-dibromnaphthol, dissolved in an alkaline solution.

HCl precipitates the free acid from a hot and concentrated solution of the soda salt; soluble in hot water, with a scarlet color.

Azodinitroxybenzole-paramidosulphoxylnaphthalene,

$$C_6H_2(NO_2)_2(OH) - N = \overset{1}{N} - C_{10}H_5(\overset{4}{H}SO_3)NH_2.$$

Produced by combining equal molecules of diazodinitrophenol with an alkaline solution of naphthionic acid.

Red-brown dye, easily soluble in water.

Parazosulphoxylnaphthalene-beta-naphtholdisulpho acid,

$$C_{10}H_6(HSO_3) - N = N - \beta\text{-}C_{10}H_4(HSO_3)_2OH.$$

Obtained by allowing equal molecules of diazonaphthionic acid and beta-naphtholdisulpho acid to react upon one another. Crimson dye, very soluble in water.

With this compound ends all I have to say to-night, but I hope to be able, at a later date, to give you a fuller account of the compounds I have just described.

XLIX.—On Wilkinson's Process for the Manufacture of Illuminating Gas from Wood.

By Charles A. Doremus, M.D., Ph.D.

Though many substances have, from time to time, been suggested as proper materials from which to procure illuminating gas when subjected to destructive distillation, none seemed to equal coal, either in the quality of gas yielded or in the economy of manufacture. Fats, factory refuse, oil, petroleum have all even now a more or less extended use, and wood is frequently resorted to.

Practical difficulties, however, have always stood in the way of its more general employment. The moisture even in the harder varieties of wood causes a lowering of the temperature of the retorts to such a degree as to largely increase the yield of tar, pyroligneous acid, and gas liquor generally. Besides this, the water, by diminishing the heat, renders the amount of gas produced very small, while the oxygen it contains goes to augment the carbonic acid, the quantity of which may even exceed twenty-five per cent. of the gas. This large amount of carbonic acid necessarily diminishes the illuminating properties of the gas, or as it is commonly expressed, "kills the light." Its removal is therefore requisite, and the cost of purification increased. Except, therefore, in few cases, wood as a source for gas has been practically abandoned.

For several years past it has been customary in some gas works to push the heat in the coal gas retorts, and obtain thereby three or four thousand feet more gas to the ton of coal, but of a very low candle power, however. This poor gas was then, after purification in the usual way, carburetted either by naphtha vapor or "fixed" naphtha vapor, or by cannel gas. A very excellent quality of gas was thus made, and at a low rate.

The first instance of the use of such a process in this country, we believe, was with the company working under Tessié du Motay's patents, in Buffalo. It was proposed by this company to manufacture water gas and enrich it by means of carburetters placed in each house. The danger of the oil (gasoline) was recognized by the insurance companies, and the "*binary*" process of making gas was then inaugurated by Dr. Wilkinson, at that time (1872) chemist for the company. With some alterations this process is in use in all works where gas is enriched.

But coal gas manufacture was destined to a more radical change than this, in the adoption of the many processes for the production of

water gas subsequently enriched by naphtha. The cost of gas is hereby so greatly reduced that it seemed as if no better method could be suggested. Supplying a gas brilliantly white when burnt, of high gravity, affording great benefit, therefore, to consumers, the projectors of the new enterprises have already reaped, at least in New York, a goodly harvest.

But older companies could not abide such an invasion of their territories without remonstrance, and though naturally the competition at first caused fierce disputes, it ended as usual in a coalition.

It was during the heat of battle that the method we are to describe was invented. From an intimate acquaintance with all the methods in use, and especially those of coal and water gas, and the advantages and disadvantages of the several processes, Dr. A. W. Wilkinson, chemist of the Mutual Gas Light Company, devised the following plan, which was first tried experimentally at the works, then operated with several benches, and finally adopted on a large scale.

The ordinary clay retort of the gas works, but slightly modified, answers, though in subsequent experiments a somewhat different shaped retort was used, the retort being provided with a fall or "boot."

The essential feature of the process consists in reducing the carbonic acid to carbonic oxide, and at the same time of getting rid of all tar, acids and waste products. This is accomplished by forcing the gas through a bed of red hot charcoal. After the first charge of wood has been carbonized, the charcoal, instead of being drawn as with coke, is shoved back in the retort. The gas made from the second charge is therefore obliged to pass through this layer of red hot coal to reach the stand pipe at the rear of the "through" retort. The heat is pushed to get as large a yield of gas as possible, and the reduction of the carbonic acid correspondingly facilitated.

The water in the wood is also an active agent, since in this superheated state it forms water gas with the aid of the charcoal. The gas needs but slight purification. Nitrogen in the form of ammonia is virtually absent; little sulphur exists in any form, neither sulphuretted hydrogen nor carbon bisulphide being found, except in traces, while of tar there is not a trace.

To prevent too great an accumulation of charcoal, the retorts are drawn twice a day.

Fifty-three thousand eight hundred and thirty-two cubic feet of gas are produced from a cord of wood costing $5.25 per cord of 3,300 lbs., as computed from the average of six months.

The quantity of gas alone is thus four times as great as that which can be obtained from coal, costing an equal sum per ton as does wood per cord.

The crude gas has the following composition, as analyzed at the works by myself:

Hydrogen	44.10
Marsh gas	5.40
Carbonic oxide	33.75
Illuminants	none
Carbonic acid	10.50
Nitrogen	6.00
Oxygen	0.25
Ammonia	none
Sulphuretted hydrogen	none
	100.00

It is still customary with the Mutual Company to manufacture a poor quality of coal gas, which is, along with the wood gas, afterwards carburetted, and in which form it is termed "commercial" gas, and has a high candle power. An analysis of the coal gas, taken from the company's records from an analysis made at the works, shows it to be composed of:

Hydrogen	30.50
Marsh gas	41.00
Carbonic oxide	6.00
Illuminants	2.00
Carbonic acid	3.00
Nitrogen	16.00
Oxygen	1.50
Ammonia	trace.
Sulphuretted hydrogen	trace.
	100.00

The yield of coal gas is 14,645 cubic feet per ton of coal, costing $5.00. From this sum we must deduct the price received for coke, tar, and gas liquor.

Prior to admixture with naphtha vapor, the coal and wood gases are purified and passed to the storage holder. From this the gas enters an illuminator, so constructed that the naphtha running in is converted into vapor by steam heat, and thoroughly mixed with the gas. From the illuminator, the mixture of gas and vapor passes into super-

heated retorts, to be "fixed." 4.5 gallons of naphtha are used for every thousand feet of "commercial" gas.

As the naphtha is of good quality, no purification of the resulting gas is needed other than passing it through a coke box to remove any liquid naphtha.*

One hundred volumes of the "commercial" gas of the Mutual Company consists, at present, of 21 volumes of wood gas, 37.4 volumes of coal gas, and 41.6 volumes of naphtha gas.

An analysis of the "commercial" gas, showed it to contain :

Hydrogen Marsh gas	56.75
Carbonic oxide	11.25
Illuminants	15.25
Carbonic acid	1.00
Nitrogen	15.00
Oxygen	0.75
Ammonia	none.
Sulphuretted hydrogen	none.
	100.00

This analysis shows also, how closely the composition can be determined by separate analyses of its components, and how, by the speedy method of gas analysis introduced by Dr. Wilkinson, in use not only in the Mutual but other gas works, a complete control of each and every step in the process of manufacture is obtained. As the method has been fully described in the *London Gas Light Journal*, for August, 1877, but this brief allusion to it seems required. An addition was made in 1879 to the process whereby nitrogen could be determined and an account published in the *American Gas Light Journal*, of that year. The rapidity with which an analysis can be made, and the simplicity of the various steps, give it a decided advantage over other methods.

No new process of manufacture stops with the application of any single scientific discovery ; the adoption of wood, therefore, instead of coal, required several changes in the management of the retorts.

The want of coke for firing was the first requirement that made itself felt. Coke might, of course, be purchased from gas works, manufacturing by the older methods, but wood gas could only thus be manufactured in one or two of the larger cities.

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* Traces of SI_2 are sometimes observable.

The furnaces were at the Mutual Works, therefore, supplied for a time from the coal benches; but, finally, grates were constructed, to allow the use of "pea" anthracite. The employment of hard coal was only feasible by an increased draught; but to obviate the use of a blower, yet accomplish this result, the following device was adopted.

At the base of the fire pot, an iron tube is inserted, having a blind end. This serves, on being heated red hot, by the fire, as a superheater for a jet of steam driven in through a central iron pipe, and passing nearly to the blind end of the exterior tube. The steam thus superheated passes next through a small injection pipe into the fire. A draught of air is drawn into the fire by this injector, and the combustion greatly accelerated. The steam also decomposes in presence of the coal, water gas is formed in abundance, and an intense heat, under absolute control, is attained.

The heat is greatly increased, too, by another ingenious device. Over the benches stretches a long, wrought iron tube, some two feet in diameter, and open at each end. The hot gases from the furnaces impinge upon this, heating the contained air. By means of suitable pipes, this heated air is drawn down by the steam injectors, and forced into the fires. A hot blast is thus procured. The saving of a dollar per diem for each fire, results from the combined use of anthracite and hot blast, over the old system of coke fires.

As regards the relative cost of "poor" coal or wood gas, it can be stated at 20 cents per thousand for coal to 9.9 cents per thousand for wood. Not only the four times greater amount of gas yielded enters in this calculation, but the large decrease in expense thereby caused in the less number of hands employed, and also the less cost of purification of wood gas made by this method. In the calculation of cost of coal gas the drawbacks in ammonia, tar, etc., have been considered. With wood there are none of these. But the Mutual Gas Light Company contends that it is a gas manufacturer, and therefore does not base its business on side issues.

After this brief outline of the special features of the mode of manufacture, we desire next to call attention to some rather remarkable facts developed in the chemical analysis of the "commercial" product. We have already detailed the analyses of the several constituents of the "commercial" gas, and shown how closely the analysis of the merchantable article agrees with what would be the theoretical result of mixing them in the proportions actually carried out on an enormous scale at the Mutual Works.

In a paper read before the American Association in Boston, August, 1880, Dr. E. G. Love, City Gas Examiner, reports the composition of the various gases sold in New York city.

Besides these, four other analyses of the Mutual gas are given; three made by Dr. Love, and one by Mr. H. C. Bowen, intended to show that there is no material difference in the quality of the gas made by the use of wood from that of coal. These were reported in the *American Gas Light Journal*, of Oct. 2, 1880. We insert both tables:

TABLE I.

CONSTITUENTS.	Manhattan Co.	Harlem Co.	Metropolitan Co.	N.Y. Mut'l Co.	N. Y. Co.	Municipal Co.
Hydrogen	45.79	46.53	35.41	10.57	27.14	26.25
Marsh gas	39.01	42.38	42.66	41.75	25.35	28.91
Carbonic oxide	6.31	3.14	9.17	9.53	26.84	27.12
Illuminants	6.38	6.31	7.41	15.41	14.63	15.80
Nitrogen	2.51	0.50	5.35	20.69	2.87	1.92
Carbonic acid	.....	1.08	.....	1.51	3.02	.....
Oxygen	.....	0.06	.....	0.54	0.15	.....
Sulphuretted Hydrogen	.....	trace	.....	trace	.....	.....
	100.00	100.00	100.00	100.00	100.00	100.00

TABLE II.

	I. July 16, 1880.	II. Aug. 6, 1880.	III. Sept. 8, 1880.	IV. Nov. 27, 1877.
Hydrogen	9.65	9.32	12.75	7.53
Marsh gas	43.55	42.49	39.21	48.63
Carbonic oxide	8.63	7.64	12.33	6.70
Illuminants	15.55	15.45	15.22	14.43
Nitrogen	19.92	22.79	19.36	19.85
Carbonic acid	1.48	2.16	0.89	
Oxygen	1.22	0.15	0.24	2.86
Sulphuretted Hydrogen	.....	.....	trace	
	100.00	100.00	100.00	100.00

Table No. I. differs quite widely in its statements, as published in the *Gas Light Journal*, from the way it was reported in the daily press at the time of the Boston meeting, four of the six analyses being much modified—two, however, being retained in exactly their original shape.

Thus with the Mutual gas the hydrogen, from being 28.87 per cent. falls to 10.57 per cent.; marsh gas rises from 22.95 to 41.75; carbonic oxide falls from 27.19 to 9.53, and nitrogen rises from 3.24

to 20.69 per cent. We are at a loss to explain these variations, especially as the quantity of illuminants is not modified. The gravity also remains as fluctuating between 0.703 and 0.808. The sulphur is 7.28 grains per 100 cu. ft., and the ammonia 82 grains per 100 cu. ft., in both analyses.

These discrepancies are, in comparison with the analyses of the commercial products of other companies, particularly noticeable. Yet Dr. Love has taken pains to show, by Table No. II., that analyses of the Mutual gas, ranging over a long interval, demonstrate its composition to be nearly constant. Thus, in comparison with other gases, the carbonic oxide was first stated to be 27 per cent., an amount in excess of that in any water gas enriched by naphtha, and a fact which does not accord at all with the process of manufacture of the Mutual gas, since we have shown that at least one-third is of a low grade of coal gas, which would contain about 6 per cent. carbonic oxide, and another third wood gas, with 30 per cent. Were these two gases mixed and distributed in equal proportion, there could only be 18 per cent. carbonic oxide, while as they form but 60 per cent. of the "commercial" gas, there would at most be but 10.8 per cent. of carbonic oxide. The analyses of Tables I. and II. agree to this state of things.

We are surprised also that a coal gas, such as that sent out by the Manhattan Company, should only contain 1.19 per cent., as in the first report. In Table I. it stands 6.31 per cent. Though in a foot note Dr. Love states: "I find considerable variation in composition, especially in those gases enriched by naphtha," we can hardly imagine them to take such curious fluctuations, since the process of manufacture precludes them.

However accurate such a method of analysis as Bunsen's may be, can it not be replaced with advantage by one which, though less correct, allows by the rapidity of execution, duplicate analyses, and thus gives a knowledge of the average composition of a commercial product? From personal experience, we know how tedious an analysis is, and how liable to error from mistakes, not only in the various steps of the method, but the subsequent calculations regarding temperature, pressure, moisture, etc., when carried out as indicated by Bunsen.

In Watt's Dictionary of Chemistry, **2**, 1036, we find the following:

"The effect of continuing the distillation too long, is that gases of a very feeble illuminating power, are evolved together with

nitrogen, which, when once mingled with the combustible gas, cannot be removed by any known method, and must seriously impair its illuminating power." We have shown, not only by our own analysis, but by Dr. Love's, that the Mutual "commercial" gas contains about 15 to 20 per cent. nitrogen. That this is not present as air, is seen from the only trivial quantity of oxygen. The nitrogen must have gained access, in great measure, from the fires around the retorts, as well as in small quantity from the leakage of air, the oxygen in the latter case being consumed in the retorts.

By an adjustment of the exhaust, the company attempts to keep the proportion of nitrogen in the "commercial" gas at 15 per cent., and there is not much variation from this figure.

No other New York company furnishes street gas with so high a percentage of a neutral gas.

According to Dr. Love's analysis, and his statement of the various candle powers, as given in Table III., the Mutual ranks as containing ten times as much nitrogen as the Municipal; yet, both having the same amount of illuminants, it is only three candle power lower. From photometric measurements at the College of the City of New York, the Mutual gas was found, on November 27th, to stand 25.5 candle power, and had 17 per cent. nitrogen.

TABLE III.

COMPANY.	Hydrogen.	Marsh Gas.	Carbonic Oxide.	Total Non-Illuminants.	Illuminants.	Nitrogen.	Carbonic Acid.	Oxygen.	Candle Power.
Manhattan.....	45.79	39.01	6.31	91.11	6.38	2.51	....	....	19.76
Harlem	46.53	42.38	43.14	92.05	6.31	0.50	1.08	0.06	17.59
Metropolitan..	35.41	42.66	9.17	87.24	7.41	5.35	....	....	20.33
N. Y. Mutual..	10.57	41.75	9.53	61.85	15.41	20.69	1.51	0.54	26.53
New York	27.14	25.35	26.84	79.33	14.63	2.87	3.02	0.15	24.35
Muncipal	26.25	28.91	27.12	82.28	15.80	1.92	....	....	29.68

According to these facts, the old impression that the presence of nitrogen is destructive to the light-giving properties of street gas, must fall, or whatever holds goods for coal gas, is not found to follow in coal gas enriched by naphtha. Never before has gas been furnished in New York, of such brilliancy, as at present. Each company charges $2.25 per thousand. Let us suppose the Mutual Company delivers 3,000,000 cubic feet per diem; 15 per cent. of this, or 450,000 cubic feet, is nitrogen which, at $2.25 per 1,000, gives $1,023.50 per diem clear profit. This percentage of nitrogen does

not seem to cause any smoking of the flame; the company receives no more complaints on this score than do others. The consumption of naphtha is always about 45 gallons per 1,000 cubic feet of "commercial" gas, a quantity below that required in other gas works.

We specially desire, therefore, in connection with the description of the wood gas process, to point out these peculiarities regarding nitrogen, trusting new experimentation will develop more clearly the reasons for these phenomena.

Reports on American and Foreign Patents Relating to Chemistry.

American Patents.

Condensed from the Official Gazette of the **U. S. Patent Office**, by ARNO BEHR.

Dec. 7, 1880.

235,070.—*Process of treating wood, etc.* CHARLES B. CARTER.

A current of steam is passed over the wood, which has been subjected to distillation in a retort.

235,143.—*Manufacture of salt.* WILLIAM W. ELMER.

Brief: The object of the invention is to reclaim and purify "trash" salt, which accumulates about packing-houses, and for obtaining pure salt from old brine, and from impure salines.

235,148.—*Apparatus for condensing fumes.* AMOS E. GRIFFITHS.

235,170.—*Art of separating vegetable fibres from animal fibres.* GEORGE M. and ALFRED L. RICE.

The acid to be used is mixed with sawdust, or the dust of rags, and in this comparatively dry or mealy condition, more evenly distributed among the material to be treated.

235,193.—*Manufacture of artificial indigo.* ADOLPH BAEYER.

The dye-stuff is produced by the action of ferrous sulphate upon the sulpho-compound of orthonitrophenylpropiolic acid.

235,202.—*Sugar washing process and apparatus.* JOHN V. V. BOOREAM.

Mechanical process of preparing raw sugar for treatment, in a centrifugal machine.

235,203.—*Carbon pencil for electric lights.* JULIUS E. BRAUNSDORF.

Claim: A carbon pencil, provided with a central metallic conducting tube, filled with non-conducting material, for increasing or coloring the light.

235,231.—*Manufacture of carbonate of magnesia.* FREDERICK GUTZKOW.

The object of obtaining it in a light and flocculent form, is reached by "heating pulp of magnesium hydrate, and forcing carbonic acid gas through it."

235,310.—*Vegetable fibre from prime leaves.* JOHN GEORGE STEVENS.

Dec. 14, 1880.

235,345.—*Fabrication of sugar.* MIGUEL DE LA VEGA and LUIZ D'OLIVEIRA.

Application of cold for the separation of sugar from its solution.

235,365.—*Asphaltum paint.* ARCHIBALD K. LEE.

235,389.—*Pyrometer.* ROBERT SPENCER.

235,487.—*Fumigating compound.* ANN ELIZA ARNOLD.

A mixture of sulphur, chloride of lime and nitre, for preserving food by fumigation.

235,488.—*Manufacture of dye-stuff, or coloring matter.* ADOLPH BAEYER.

Treating artificial indigo with sulphurous acid, followed by a mineral acid.

235,497.—*Selenium cell.* ALEXANDER G. BELL and SUMNER TAINTER.

235,521.—*Distilling and rectifying apparatus.* EDWARD FOX.

235,590.—*Selenium cell.* SUMNER TAINTER.

Dec. 21, 1880.

235,615 —*Baking powder.* CHARLES E. AVERY.

Acid lactate of calcium with an alkaline bicarbonate.

235,616.—*Process for treating selenium to increase its electric conductivity.* ALEXANDER G. BELL and SUMNER TAINTER.

235,633.—*Composition for preventing incrustation of boilers.* HERMANN HEIMANN.

Roasted and ground coffee beans.

235,644.—*Process of ornamenting the surfaces of hard rubber with colors.* FRED. A. NICKERSON.

235,784.—*Process of extracting silver from ores.* GEORGE A. KOENIG.

The ores are treated with a solution of chloride of sodium and chlorine under heat and pressure.

235,820.—*Apparatus for the decomposition of chloride of calcium.* ERNEST SOLVAY.

Dec. 25, 1880.

235,858.—*Process of separating plumbago from its ores.* HIRAM T. DREHER.

Disintegrating the ore by the combined action of heat and water, crushing and rolling the disintegrated material, and separating the flakes from the ore.

235,871.—*Explosive compound.* WILLIAM HEICK.

A mixture of honey and glycerine treated with nitric and sulphuric acid, chlorate of potash, nitrate of potash, prepared sawdust and prepared chalk.

235,909.—*Composition from mineral wool for journal bearings.* GEORGE F. SENTER.

Mineral wool, plumbago and water glass, with or without paraffine.

235,923.—*Tanning extract.* HIRAM L. WILCOX.

A preparation from *polygonum amphibium.*

236,034.—*Factitious material to imitate ivory, horn, etc.* JOHN W. HYATT, CHARLES S. LOCKWOOD and JOHN S. STEVENS.

"A material consisting wholly or in part of bone-dust and a suitable water-repellant, welded by heat and pressure."

236,037.—*Assay furnace.* WILLIAM E. JUDSON.

236,051.—*Manufacture of chloride of zinc.* EDWARD T. MALLETT, Jr.

A mixed solution of sulphate of zinc and chloride of sodium is artificially cooled from the surface.

236,065.—*Preserved wood.* HERMANN T. MUELLER.

"Wood impregnated with sulphate of barium and chloride of sodium."

236,083.—*Manufacture of artificial slate.* HEINRICH REINHOLD.

236,095.—*Burner and apparatus for burning petroleum.* ERNST SCHULTZ.

236,115.—*Composition for use in tanning.* HEINRICH TRENK.

A concentrated solution of crude tartar, with a small quantity of chloride of zinc.

Foreign Patents.

Condensed from R. BIEDERMANN'S Report to the German Chemical Society, by OTTO H. KRAUSE.

HÖRDER BERGWERKS UND HÜTTENVEREIN HÖRDER UND RHEINISCHE STAHLWERKE, Ruhrort: *Manufacture of bricks by the Thomas process, from lime free from magnesia.* (Germ. P., No. 10631, January 8, 1880, being additional Patent to Germ. P., No. 5869, of October 5, 1878.)—Small quantities of fritting substances, as silicic acid, clay, ferric oxide, are added to the limestone.

BOCHUMER VEREIN FÜR BERGBAU UND GUSSSTAHLFABRIKATION, Bochum: Improvements upon Germ. P., No. 5869, *for manufacturing basic bricks.* (Germ. P., No. 10683, Oct. 29, 1879.)—Litharge, minium or manganic oxide are added to the lime or dolomite.

H. A. BERTHAUT, Paris: *Manufacture of aluminium and magnesium.* (Engl. P., No. 4087, Oct. 9, 1879.)—Electrolysis of molten aluminium-sodium chloride, or of magnesium chloride, by means of a current from a dynamo-electric machine.

G. W. BREMNER, London: *Adhesive compound from aluminium phosphate.* (Engl. P., No. 3579, Sept. 6, 1879.)—Native aluminium phosphate, rendered soluble by heating and the action of sulphuric acid, is mixed with 20 per cent. gypsum, and silicate of soda added.

ANTON GINARDONI, Vienna: *Bleaching of jute and similar fibres, as well as of the fabrics made from them.* (Engl. P., No. 3359, Aug. 20, 1879.)—Consists in successively treating them with a solution of potassium dichromate, acidified with sulphuric acid and chloride of lime, or an alkaline hypochlorite.

R. C. ANDERSON, Woodgreen: *Galvanic battery.* (Engl. P., No. 3436, August 26, 1879.)—Sulphuric acid or salt for the zinc; oxalic acid and potassium dichromate for the carbon.

A. H. HASSALL and O. HEHNER, London: *Preparation of extracts from tea, coffee, etc.* (Engl. P., No. 3437, August 26, 1879.)—Infusion of tea is distilled, and the volatile and aromatic substances concentrated by redistillation, are added to the extract obtained by evaporating the infusion.

C. M. TESSIÉ DU MOTAY and AUGUSTE J. ROSSI, New York: *Improvements in the methods of producing cold for the manufacture of ice.* (Germ. P., No. 11036, February 8, 1880.)—Noticed under American Patents, this JOURNAL, **2**, 296.

P. A. PARLIER, Paris: *Electrodes for electric light.* (Engl. P., No. 3355, Aug. 20, 1879.)—Tubes of steel containing compressed magnesia, or dolomite, lime, alumina free from silicates, or the carbonates of strontium and barium.

H. PROSCHWITZKY, Stettin: *Manufacture of ammonium sulphate.* (Germ. P., No. 10957, February 10, 1880.)—Retorts are charged in alternate layers with leather waste and crude limestone. The gases evolved are passed through empty vessels, to separate tar, etc., and are then absorbed by sulphuric acid.

ROBERT WEARE, Manchester: *Manufacture of carbon for filtering.* (Engl. P., No. 3879, Sept. 26, 1879.)—Excrement, waste matters of all kinds, sewage, are carbonized in retorts. The gases evolved are led into the fire, and the carbon used for the purpose indicated above.

W. G. GARD, Dunstable: *Evaporation and concentration of liquids.* (Engl. P., No. 3348, August 19, 1879.)—Air, dried by passing through a tower containing coke or pumice-stone moistened with sulphuric acid, is warmed and then brought in contact with the surface of the liquid to be evaporated.

F. V. WARREN, Southsea: *Lubricant.* (Engl. P., No. 4021, October 6, 1879.)—Mixture of ozokerite with fat and oil.

W. I. MENZIES, St. Helens: *Apparatus for grinding and sifting caustic alkalies.* (Engl. P., No. 4274, Oct. 21, 1879.)—The mill and sieves through which the hot alkalies are passed, can be kept heated.

N. BASSET, Paris: *Manufacture of ammonia and its salts.* (Engl. P., No. 4338, Oct. 24, 1879.)—This invention consists essentially in the preparation of nitride of boron, or combinations of it with other nitrides, and in treating it with steam at a low red heat. The hydrogen combines with the nitrogen of the nitrides and is evolved as ammonia.

R. LANCASTER, Kirkdale : (Engl. P., No. 4122, Oct. 11, 1879.)—Proposes to produce alkali by heating steam to 1,500° F., injecting it into a chamber filled with limestone, and passing the resulting gases which, according to the inventor, consist of carbonic acid and hydrogen, through melted sodium chloride.

G. S. HAZELHURST, Runcorn : *Apparatus for absorbing hydrochloric acid.* (Engl. P., No. 4233, Oct. 18, 1879.)—One or more vertical pipes filled with open brickwork through which water trickles and meets the gases entering below.

J. B. M. P. CLASSON, Paris : *Manufacture of magnesia.* (Engl. P., No. 4253, Oct. 20, 1879.)—Solution of manganic chloride resulting in the manufacture of chlorine, or ammonia chloride from the ammonia soda process, is decomposed by means of burnt dolomite instead of lime. The liquor, rich in magnesium chloride, which is obtained by several repetitions of the process, is evaporated and calcined, yielding hydrochloric acid. The magnesia is obtained by extracting the residue.

G. D'ADELSWÄRD, Paris : *Method of preparing magnesium hydrate for the manufacture of infusible bricks.* (Germ. P., No. 11321, Jan. 7, 1880.)—Dolomite is dissolved in hydrochloric acid or manganic chloride, and the solution precipitated with lime.

O. JUNGHANN and UELSMANN, Konigshütte : *Improvements in the preparation of basic furnace linings.* (Germ. P., No. 11360, Dec. 21, 1879.)—Calcic phosphate or bone ash is mixed to a paste with calcium or magnesium chloride.

W. MORGAN BROWN : *Manufacture of sulphate of lime.* (Engl. P., No. 4637, Nov. 14, 1879.)—Milk of lime and sulphuric acid run in thin streams into a suitable vessel.

H. HARMET, Denain : *Manufacture of zinc and zinc white.* (Germ. P., No. 11197, March 23, 1880.)—A mixture of zinc ore and charcoal is put into a furnace with a closed throat. The gaseous products, zinc vapor and carbonic oxide escape to heated chambers, into which air is admitted to convey the oxide of zinc produced, into settling chambers.

H. VON LIEBIG, Dinkelsbuehl : *Method of preparing a fertilizer containing a calcium-potassium-magnesium phosphate.* (Germ. P., No. 11547, Feb. 21, 1880.)—Guano, bone dust, bone ash or mineral phosphates are rendered soluble by hydrochloric acid in suitable proportions. Crude potassium or magnesium sulphate or kainite are then added to the paste.

CH. DE VANRÉAL, Paris : *Extraction of gold and silver from ores containing sulphur, antimony and arsenic.* (Germ. P., No. 10716, Nov. 25, 1879.)—The ores are heated in a current of hydrogen to remove arsenic. The residues are then roasted and treated successively with sulphuric and hydrochloric acids to remove copper and antimony compounds respectively. If silver only be present, its chloride is dissolved out by means of sodium thiosulphate. If both silver and gold are present amalgamation is employed.

L. BOBLIQUE, Paris : *Dephosphorization of iron.* (Engl. P., No. 4625, Nov. 13, 1879.)—The furnaces are lined with bauxite, to which ferric oxide, lime or magnesia may be added

JAS. M. CAREW, Clapton : *Extraction of cobalt and nickel from their ores.* (Engl. P., No. 4607, Nov. 12, 1879.)—A wet process, in which hydrochloric and sulphuric acids, sodium carbonate and ammonium sulphide are employed for the purpose of dissolving the ores, and separating the different metals in solution. Pure cobalt and nickel are finally precipitated by means of zinc.

A. L. DOUCET, Brussels : *Treatment of copper, lead and zinc ores.* (Engl. P., No. 3586, Sept. 6, 1879.)—The sulphides are heated in retorts or furnaces in a current of hydrochloric acid gas to convert them into chlorides. When this has taken place the temperature is raised, air blown in, and the volatilized chlorides received in condensing chambers. The solution of the chlorides is effected with the aid of a thermo-electric pile which is also employed for the separation of the zinc. Other processes and reactions are proposed for ores which also contain silver.

G. C. TREWBY and H. W. FENNER, Beckton : *Distillation of coal tar.* (Engl. P., No. 3613, Sept. 9, 1879.)—Steam is injected through an open coil in the still, when its contents have reached a temperature of 212° F.

A. D'ANDIRON and G. WEGELIN, Mülhausen : *Production of black dyes.* (Engl. P., No. 4123, Oct. 11, 1879.)—Mixtures of aniline and its homologues in different proportions. Such mixtures are said to produce blacks which do not assume a greenish hue, as is the case when pure aniline is employed.

E. JACOBSEN, Berlin : *Method of preparing benzoic acid, benzoic ether and benzoic anhydride, together with organic acid chlorides, from benzotrichloride or dichloride in presence of certain metallic salts.* (Germ. P., No. 11494, Dec. 7, 1879.)—Various processes and reactions, usually in presence of zinc chloride or acetate, are described, viz : Glacial acetic acid heated and benzotrichloride added, yields hydrochloric acid and chloride of acetyl. Benzoic acid is obtained from the residue by extracting it with sodium carbonate and precipitating with hydrochloric acid.

Acetate of zinc and benzotrichloride yield acetic and benzoic anhydrides.

Acetic acid, under the influence of chloride of acetyl, gives acetic anhydride.

Benzotrichloride can be resolved into benzoic acid without simultaneous production of chloride of acetyl, by heating it in a vessel supplied with a returning condenser, the water necessary for the formation of benzoic acid being added gradually.

Benzodichloride and acetic acid yield benzoic aldehyde and chloride of acetyl.

Benzotrichloride and dichloride also react upon the ethers of the carbon acids forming, with acetic ether for instance, benzoic ether in one case and benzoic aldehyde in the other, together with acetyl and ethyl chlorides. A similar result is obtained by the action of benzotrichloride and dichloride upon the alcohols of the fatty series. The zinc chloride can be replaced by the chlorides of antimony or copper.

J. B. PASCAL, Lyons : *Soup extract.* (Germ. P., No. 11500, March 10, 1880.)—Beef is boiled in the broth of vegetables, the fat skimmed off, salt added, and he whole reduced to the consistency of a syrup.

W. LANGWELL, Sheffield : *Treatment of porcelain and stoneware.* (Engl. P., No. 4723, Nov. 20, 1879.)—Produces iridescence upon the objects, by exposing them in the furnace to the vapors from a mixture of one hundred parts stannic chloride, six parts strontium nitrate and six parts barium nitrate.

C. HEINZERLING, Frankfort on the Main : *Improvements upon Heinzerling's rapid tanning process.* (Germ. P., No. 10665, Dec. 24, 1879, being additional Patent to Germ. P., No. 5298, Nov. 3. 1878.)—Claims chromium sulphate and chloride, also aluminium chloride. The Patent also relates to a grease composed of wax, rosin, spermaceti or a caouchouc-like substance, obtained by treating oils with 10-20 per cent. of chloride of sulphur.

FR. KNAPP, Braunschweig : *Method of preparing ferric salts for tanning purposes.* (Germ. P., No. 10518, Dec. 25, 1879, being additional to Germ. P., No. 444, June 21, 1877.)—Equivalent quantities of sulphuric acid and nitrate of soda are added to a solution of sulphate of iron, whereby the soda of the nitrate enters as a constituent of the ferric salt formed. The tanning is effected by means of the precipitate which this salt produces with albumens from different sources, blood for instance.

R. C. M. DE MOLON, Paris : *Fertilizer.* (Engl. P., No. 3928, Sept. 30, 1879.)—Pulverized calcium phosphate is piled in layers with seaweed, and allowed to ferment. Excrements, fish waste, etc., may be added.

ALEX. MANBRÉ, Liverpool : *Treatment of the residues resulting from the extraction of starch from maize.* (Engl. P., No. 3996, Oct. 4, 1879.)—Treats with sulphuric acid to convert the starch left in them into glucose, which is then subjected to fermentation. What remains is steamed and strongly pressed to obtain oil.

E. DE WERCHIN, Meslay : *Preservative and insecticide.* (Engl. P., No. 4523, Nov. 6, 1879.)—Composed of oil, camphor and carbolic acid.

W. JEYES, Birmingham : *Soap.* (Engl. P., No. 4740, Nov. 21, 1879.)—To which anthracene or naphthalene is added just before finishing it.

MATTHEW BLAIR, Sunderland : *Combustible.* (Engl. P., No. 3725, Sept. 17, 1879.)—Slate and coal are pulverized, mixed with tar, whale oil, petroleum, etc., and pressed into blocks.

GABRIEL DEHAYNIN, Paris : *Apparatus for generating "carbon hydroxide."* (Engl. P., No. 4611, Nov. 12, 1879.)—This strange specification contains the description of a retort for decomposing steam with coals heated to redness.

A. J. CAZET *et al*, Paris : *Method of rendering liquids, such as petroleum, molasses, etc., hard.* (Engl. P., No. 4619, Nov. 13, 1879.)—See this JOURNAL, **2**, 300.

F. MARQUARDT, Vienna : *Manufacture of peptone, yeast, etc.* (Engl. P., No. 3706, Sept. 16, 1879.)—Leguminosæ, corn, and especially the residues from breweries, are treated with very dilute solutions of acids or sodium chloride, whereby the soluble protein bodies are converted into peptone.

JACOB RAINER, Vienna: *Peptone from vegetable matters.* (Engl. P., No. 3776, Sept. 19, 1879.)—100 pts. of germs from sprouted malt are macerated in a solution of $\frac{1}{10}$ pt. pepsine, 4 hydrochloric acid and 8 sodium chloride, in 300 pts. water. After 24 hours the acids are neutralized, and the salts precipitated from the evaporated solution by means of alcohol.

J. WICKERSHEIMER, Berlin: *Method of preserving fresh meat.* (Germ. P., No. 11530, March 14, 1880.)—A solution containing 36 grms potash, 15 grms common salt and 60 grms alum, in 3 liters of water, is heated to 50° C. and mixed with a second solution, containing 9 grms salicylic acid in 45 grms methylic alcohol or 250 grms glycerine. This mixture is injected into the animal before cutting it open. 40–100 grms per kgrm of live weight of the animal are to be used. Another solution is mentioned for preserving corpses and animals which are not intended to be used as food.

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